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EMISSIONS OF OXIDES OF NITROGEN FROM STATIONARY SOURCES IN LOS ANGELES COUNTY. REPORT NO. 2, OXIDES OF NITROGEN EMITTED BY SMALL SOURCES

Los Angeles County Air Pollution Control District
Los Angeles, California

September 1960

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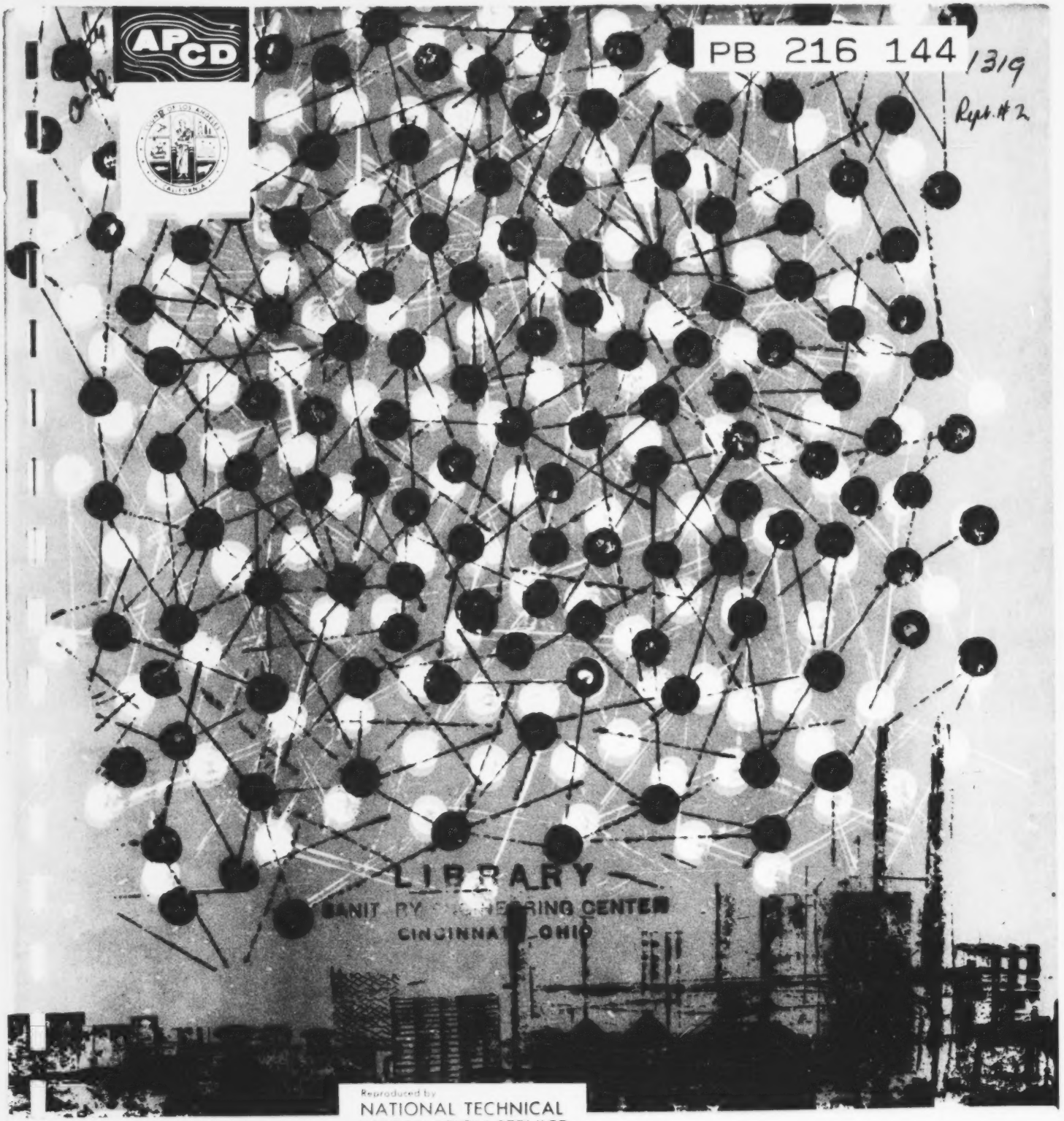

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EMISSIONS OF OXIDES OF NITROGEN FROM STATIONARY SOURCES IN LOS ANGELES COUNTY / *Report No. 2*

AIR POLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES

EMISSIONS OF OXIDES OF NITROGEN FROM STATIONARY SOURCES IN LOS ANGELES COUNTY

REPORT NO. 2

OXIDES OF NITROGEN EMITTED BY SMALL SOURCES

A JOINT DISTRICT, FEDERAL, STATE AND INDUSTRY PROJECT

Details of illustrations in
this document may be better
studied on microfiche.

SEPTEMBER 1960

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FOREWORD

In July 1959, the Committee for the Joint Project for the Determination of Emissions of Oxides of Nitrogen from Stationary Sources in Los Angeles County was formed and began its studies. The mission of the committee is to determine the total weight of oxides of nitrogen emitted into the atmosphere each day from non-moving sources of air pollution.

In classifying sources of air pollution for the purposes of study and analysis, the Los Angeles County Air Pollution Control District has separated moving sources from stationary sources. Moving sources, which alone are estimated to produce over 400 tons per day of oxides of nitrogen, are the subject of other studies and are not considered in this series of reports.

The first report, issued in February 1960, describes the background and initiation of the project, the role of oxides of nitrogen in the air pollution problem, the anticipated program for the project and the sampling and analytical procedures to be used. The program was organized so that the various sources would be studied by groups classified according to the discharge of oxides of nitrogen per unit of equipment and were defined as follows:

Large Sources	-	those emitting over 100 pounds per hour
Medium Sources	-	those emitting 5 to 100 pounds per hour
Small Sources	-	those emitting less than 5 pounds per hour

It was estimated prior to the initiation of the project that all stationary sources produced 294 tons per day of oxides of nitrogen, of which large sources contributed 203 tons, medium sources 62 tons and small sources 29 tons.

This second report discusses the evaluation of data obtained from tests made on small sources. Subsequent reports will cover the discharge of oxides of nitrogen from medium and large sources.

Oxides of nitrogen produced in and discharged from various units of equipment consist essentially of nitric oxide (NO) and nitrogen dioxide (NO_2). Although other oxides of nitrogen exist in or are naturally present in the atmosphere,[1] they are either unreactive at atmospheric temperatures or exist in such minute quantities as to be unimportant or

irrelevant to this study. For these reasons, throughout this and succeeding reports the term "NO_x" will be used to refer to the sum of emissions of nitric oxide and nitrogen dioxide, calculated as NO_2.

ROBERT L. CHASS

Project Director

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I. SUMMARY OF FINDINGS

From tests conducted, it was calculated that the total weight of NO_x emitted into the atmosphere in Los Angeles County from all small stationary sources averages 59 tons per calendar day during the six months' heating season (November through April) and 32 tons per calendar day during the remainder of the year. The weighted average of these amounts is 46 tons per calendar day, a figure which is somewhat higher than the estimate made prior to the initiation of the project (29 tons per day).

Of this weighted average daily discharge of NO_x from all small stationary sources, slightly over half (27 tons) originates from gas-fired commercial and domestic appliances and the remainder (19 tons) from small industrial sources. Most of the NO_x discharged from small industrial sources (approximately 16 tons per calendar day, weighted average) is produced by boilers of less than 500 horsepower rating. Most of the seasonal variations in the total weight of NO_x discharged from small stationary sources are ascribable to the nearly two million residential space heaters, which vent 19 tons per calendar day during the heating season and none during the remainder of the year. A summary of NO_x emissions for all small stationary sources appears in Table I.

Concurrently with analyzing vent gas samples for this project, the personnel of the laboratories of the participating agencies conducted investigations of the sampling and analytical techniques employed. These studies showed that the chosen procedures and techniques produce reliable analytical results. During the course of these investigations, a previously unknown phenomenon was discovered, that some of the NO_x seems to disappear from flue gas samples taken from oil-burning power plant boilers when the samples are left standing with no absorbing solution in the bulbs. This phenomenon is being investigated further. Detailed results of the investigation will be published in subsequent reports. Preliminary studies appear to indicate that NO reacts with SO_2, reducing the quantity of NO_x and forming SO_3.

TABLE I

EMISSIONS OF OXIDES OF NITROGEN FROM SMALL STATIONARY SOURCES IN LOS AN
AS OF END OF 1960

Source	Census[a]	Number of Tests Evaluated	Range of NO_x Concentrations in Vented Gases P.P.M.[b]			Unit Emission Factors		
			Minimum	Average	Maximum	Average Pounds Per Hour	Average Pounds Per Million Btu	Average Pounds Per Ton of Produc
A. GAS APPLIANCES								
1. Space heaters								
a. Domestic	1,900,000							
b. Commercial	371,000	7	34	50	62	0.0087	0.093	
2. Water heaters								
a. Domestic	1,848,000	5	4	50	96	0.010	0.18	
b. Commercial	186,000	2	18	50	83	0.010	0.18	
3. Ranges								
a. Domestic	1,727,000	3	8	15	33	0.0033	0.055	
b. Commercial	38,220					0.0033	0.055	
4. Refrigerators	199,000	2	1	5	8	0.0002	0.027	
5. Clothes driers								
a. Domestic	114,000	3	1	2	3	0.0007	0.041	
b. Commercial	4,520	1	1	4	9	0.067	0.11	
6. Miscellaneous	14,200	1		6		0.020	0.071	
TOTALS FOR GROUP A		24						
B. METALLURGICAL FURNACES								
1. Metal melting furnaces								
a. Direct electric-arc type	23	3	2	17	77	2.4		
b. Crucible and pot-types								
(1) For aluminum	475	2	13	16	19	0.037	0.064	0.82
(2) For brasses & bronses	280	2	45	52	58	0.073	0.071	0.95
(3) For lead	50	2	4	8	12	0.09	0.052	0.30
(4) For magnesium	111	1		28		0.0052	0.040	0.10
c. Reverberatory types								
(1) For aluminum	76	2	2	10	18	0.044		0.12
(2) For brasses & bronses	23	1		84		0.32		0.40
(3) For lead	7	2	8	13	18	0.36	0.96	
(4) For zinc	5	1		78		0.24	0.38	
(5) For cast iron	14	1	136	172	207	2.2	0.18	
d. Sweat furnaces								
(1) For aluminum	30	2	9	11	13	0.045	0.15	
(2) For lead	15	1		47		0.32	0.65	
(3) For zinc	4	1		18		0.09	0.11	
e. Gray iron cupolas	44	4	8	13	15	0.65		0.12
f. Induction furnaces	--	2		0				
2. Heat treat furnaces								
a. Box type	540	1		45		0.006	0.043	
b. Salt-pot type	220	4	155	160	170		0.10	
c. Atmosphere type	55	2	3	6	12	0.009	0.050	
3. Steel mill "soaking pits"	10	2	25	30	50	0.54	0.072	
TOTALS FOR GROUP B		36						
C. NON-METALLURGICAL FURNACES & KILNS								
1. Ceramic kilns								
a. Tunnel kilns	26	5	3	24	66	0.095	0.57	
b. Large beehive kilns	10	1		85		2.7	0.14	
c. Small beehive kilns	28	1		75		1.8	0.23	
2. Boric oxide fusion furnace	2	1		2		0.012	0.005	
3. Perlite furnaces	10	1	17	19	21	0.12	0.065	
TOTALS FOR GROUP C		9						

TABLE I

FROM SMALL STATIONARY SOURCES IN LOS ANGELES COUNTY
AS OF END OF 1960

Unit Emission Factors			Usage Factors Hours/Calender Day			Total NO_x Emissions					
						Pounds/Calendar Day[c]			Tons/Calendar Day[c]		
Average Pounds Per Hour	Average Pounds Per Million Btu	Average Pounds Per Ton of Product	Winter	Summer	Average	Winter	Summer	Average	Winter	Summer	Average
0.0087	0.093		2.3	0	1.2	38,000 5,300		19,000 2,700	19 2.7	0.0 0.0	9.5 1.4
0.010	0.18				1.3	24,000	24,000	24,000	12	12	12
0.010	0.18				1.5	2,900	2,900	2,900	1.2	1.2	1.2
0.0033	0.055				0.6	3,500	3,500	3,500	1.8	1.8	1.8
0.0033	0.055				8	1,000	1,000	1,000	0.50	0.50	0.50
0.0002	0.027				4	150	150	150	0.08	0.08	0.08
0.0007	0.041				0.2	7	7	7	negl.	negl.	negl.
0.067	0.11				3.6	1,100	1,100	1,100	0.55	0.55	0.55
0.020	0.071				5	140	140	140	0.07	0.07	0.07
						76,000	33,000	54,000	38	16	27
2.4					10.2			562			0.28
0.037	0.064	0.82			6			94			0.05
0.073	0.071	0.95			6			130			0.07
0.09	0.052	0.30			15			28			0.01
0.0052	0.040	0.10			6			4			negl.
0.044		0.12			16			40			0.02
0.32		0.40			12			18			0.01
0.36	0.96				16			63			0.03
0.24	0.38				20			29			0.02
2.2	0.18				3			78			0.04
0.045	0.15				7.5			8			negl.
0.32	0.65				7			35			0.02
0.09	0.11				5			3			negl.
0.65		0.12			4			57			0.03
					--			0			0.0
0.006	0.043				15			50			0.03
	0.10				6			140			0.07
0.009	0.050				15			7			negl.
0.54	0.072				16			86			0.04
						1,400[d]	1,400[d]	1,400	0.72[d]	0.72[d]	0.72
0.095	0.57				7.3			18			0.01
2.7	0.14				2.8			77			0.04
1.8	0.23				6.9			350			0.18
0.012	0.005				24			1			negl.
0.12	0.065				12			14			negl.
						460[d]	460[d]	460	0.23[d]	0.23[d]	0.23

Continued on page 3.

B

TABLE I (CONTINUED)

EMISSIONS OF OXIDES OF NITROGEN FROM SMALL STATIONARY SOURCES IN LOS
AS OF END OF 1960

Source	Census[a]	Number of Tests Evaluated	Range of NO_x Concentrations in Vented Gases P.P.M.[b]			Unit Emission Factors		
			Minimum	Average	Maximum	Average Pounds Per Hour	Average Pounds Per Million Btu	Average Pounds P Ton of Pro
D. CHEMICAL PROCESS EQUIPMENT								
1. Phosphoric acid plants	3	2	1	2	3	0.14		
2. Sulfur recovery plants	7	1		2		0.018		0.05
3. Sulfuric acid plants (contact)	3	2	1	5	9	0.10		0.01
4. Steel chemical milling tanks	4	1		6		0.53		0.062
5. Bright dip tanks	12	2	440	450	460	0.7		
6. Crystallizers	1	1		20		0.17	0.056	
7. Spray driers	6	2		7			0.085	
TOTALS FOR GROUP D		11						
E. GENERAL INDUSTRIAL EQUIPMENT								
1. Boilers (under 500 h.p.)								
a. Firm gas rate	2,940	8		f)			0.14 (gas)	
b. Interruptible gas rate	2,234	19		f)			0.14 (gas)	
c. Fuel oil only	519	6		f)			0.49 (oil)	
2. Small refinery heaters	283	32	20	47	100	3.2	0.06	
3. Baking and drying ovens	2,800	37		25		0.1	0.08	
4. Degreasers	1,400	4	4	8	13	0.004	0.02	
5. Welding equipment	150,000			10		0.0007		
6. Incinerators								
a. 0-99 pounds per hour	432	38	7	30	65	0.065		
b. 100-499 pounds per hour	668	48	10	43	90	0.22		
c. 500-999 pounds per hour	82	10	13	28	65	0.75		
TOTALS FOR GROUP E		202	-					
F. AIR POLLUTION CONTROL EQUIPMENT								
1. Afterburners								
a. For flue-fed incinerators	250	15	13	50	63	0.10	0.08	
b. Others	300	9	4	75	87	0.15	0.05	
2. Electrical precipitators	---	2		0		0	0	
TOTALS FOR GROUP F		26						
G. MISCELLANEOUS EQUIPMENT								
1. Refinery flares								
a. Pilot	40	1		5		0.010	0.014	
b. Flare operation	40	1		25		0.010	0.065	
2. Smoke generators for meat curing	61	2	24	29	34	0.05	0.0051	
3. Galvanizing kettles	29	1		5		0.013	0.018	
TOTALS FOR GROUP G		5						
GRAND TOTALS		313						

a) In cases where total emissions from a group were found to be insignificant, no census or use factor is reported (indicated by a dash).

b) At stack conditions.

c) Data rounded off to two significant figures or to the nearest 0.01 ton. Emissions of 0.005 ton per day or less are reported as negligible.

d) Where average emis for both summer an

e) Pounds per hour pe

f) See Tables XII, XIII

TABLE I (CONTINUED)

EN FROM SMALL STATIONARY SOURCES IN LOS ANGELES COUNTY
AS OF END OF 1960

Unit Emission Factors			Usage Factors Hours/Calendar Day			Total NO_x Emissions					
						Pounds/Calendar Day[c]			Tons/Calendar Day[c]		
Average Pounds Per Hour	Average Pounds Per Million Btu	Average Pounds Per Ton of Product	Winter	Summer	Average	Winter	Summer	Average	Winter	Summer	Average
0.14					24			9			negl.
0.018		0.05[e]			24			15			0.01
0.10		0.01[e]			24			10			0.01
0.53		0.062[e]			8.5			65			0.03
0.7					6			50			0.03
0.17	0.056				8			1			negl.
	0.085				4.9			40			0.02
						190[d]	190[d]	190	0.10[d]	0.10[d]	0.10
	0.14 (gas)		2.0	0.4	1.2	3,500	700	2,100	1.8	0.4	1.1
	0.14 (gas)		14	11	12.3	20,000	16,000	18,000	10	8.0	9.0
	0.49 (oil)		11	8	9.3	13,000	10,000	11,000	6.5	5.0	5.5
3.2	0.06				22			2,000			1.0
0.1	0.08				4			1,100			0.55
0.004	0.02				5.3			21			0.01
0.0007					0.1			11			0.01
0.065					1.3			37			0.02
0.22					2.9			420			0.21
0.75					5.3			340			0.17
						40,000[d]	31,000[d]	35,000	20[d]	15[d]	18
0.10	0.08				0.5			12			0.01
0.15	0.05				12			540			0.27
0	0				--			0			0
						550[d]	550[d]	550	0.28[d]	0.28[d]	0.28
0.010	0.014				24			10			0.01
0.010	0.065				24			100			0.05
0.05	0.0051				16			23			0.01
0.013	0.018				24			8			negl.
						140[d]	140[d]	140	0.07[d]	0.07[d]	0.07
						119,000	67,000	92,000	59	32	46

d) Where average emissions only were calculated, all those figures were added in for both summer and winter conditions.

e) Pounds per hour per 1,000 pounds of HNO_3 in the tank.

f) See Tables II, III and IIII.

B

II. INTRODUCTION

The test program for this project was organized on the basis that the first group of tests would be performed on small sources--those venting less than five pounds per hour of NO_X. The following equipment had been tentatively placed in the small-source category prior to the start of the project:

1. Small boilers
2. Domestic gas-fired equipment
3. Small oil heaters (oil refineries)
4. Small incinerators
5. Drying and baking ovens
6. Ceramic kilns
7. Gray iron cupola furnaces
8. Open hearth steel furnaces
9. Induction metal-melting furnaces
10. Crucible type metal-melting furnaces
11. Afterburners
12. Stationary internal combustion engines
13. Miscellaneous
    a. Rubber curing ovens
    b. Rock wool driers
    c. Bright dip tanks
    d. Steel chemical milling tanks
    e. Arc-welding machines
    f. Nitric acid plants
    g. Sulfuric acid plants

Although it had been estimated that this class of equipment contributes approximately 29 tons per day of NO_X to air pollution, it was agreed that additional tests plus a census of the number of units of each type would be needed before a reliable calculation of the NO_X production could be made. Although data from more than 200 tests were already available, it was decided that at least 79 additional tests would be needed. Actually, 86 additional tests were made.

The method chosen for establishing the NO_X contribution for each type of equipment was to establish three sets of data: (1) a census of units, (2) an average emission factor for each type of unit, and (3) a usage factor.

The sources of census data are:

1. Los Angeles County Air Pollution Control District records.
2. Western Oil and Gas Association surveys.
3. Southern California Gas Company records.
4. Manufacturers' representatives (in the case of welding equipment).

The emission factors are based on the results of the tests conducted and are expressed in weight of NO_X per hour, weight of NO_X per million Btu, or weight of NO_X per unit weight of product or per unit weight of reactant.

The usage factor for each type of equipment represents the proportionate time the average unit of that equipment is in operation. These factors were determined from data obtained from:

1. Los Angeles County Air Pollution Control District records.
2. Individual operators of equipment.
3. Southern California Gas Company records.
4. Consumption data on welding rods and acetylene from welding supply manufacturers' representatives and from the literature.
5. Estimates made by Los Angeles County Air Pollution Control District engineers and based on experience.

Usage factors are expressed in hours per calendar day and represent the number of hours a unit of equipment discharges NO_X at the average rate expressed by the emission factor.

Although some types of equipment were found to operate only six, five or even fewer days per week, the great majority of the units in the small-source category are operated seven days per week. This majority group of equipment consists predominantly of units located in residences. Since these units also comprise the greatest single mass of contributors of NO_X in the group, all data were reduced first to a calendar week basis rather than an industrial or commercial week basis and then to a "per calendar day" basis.

The concentrations of NO_X as measured by the laboratories are reported on a dry basis at "standard conditions," which are defined as a gas temperature of $60^{\circ}F$ and a gas pressure of 14.7 pounds per square inch absolute. Since effluent gases are usually vented at elevated temperatures and since moisture contents are extremely variable,

the laboratory results of NO_x concentrations were recalculated to actual stack conditions for comparison purposes and for calculation of total production of NO_x.

For the purpose of presenting data in a manner in which related figures are listed together, the sub-classifications of equipment as shown in the tentative list were re-grouped before reporting in Table I, which summarizes the results of this part of the project.

Two of the types of units originally believed to be in the small-source category, open-hearth steel furnaces and stationary internal combustion engines, were found to produce over five pounds per hour of NO_x and were, consequently, reclassified into the next larger group. Three other kinds of units were reclassified from medium sources when analytical results showed them to be small sources: electric-arc type steel-melting furnaces, steel mill "soaking pits" and perlite-expansion furnaces. In addition, several miscellaneous types of equipment not previously classified were added to the list. Instead of being tabulated separately under the headings of "Rubber Curing Ovens" and "Rock Wool Driers," data concerning these units have been reported under the more general heading of "Baking and Drying Ovens." No tests were made to determine the NO_x production from nitric acid plants because no plant in the County is in operation at this time.

Data used in the project have been projected to the end of the calendar year 1960. This has been done both to provide a common date for a basis of comparison with data to be presented in subsequent reports and to increase the timeliness of the data presented. The fact that emission data have been related to fuel consumption increases the accuracy of this projection, as will be shown in Section IV.

III. INVESTIGATIONS OF SAMPLING AND ANALYTICAL PROCEDURES

The sampling and analytical procedures using the phenoldisulfonic acid method for determining NO_x have been reported previously in detail.[1] At the outset of this project, some difficulties were encountered in obtaining consistent results in duplicate samples. There were also some problems in obtaining good checks by different laboratories carrying out sampling and analytical procedures for the same source.

Investigations were conducted jointly by the personnel of several of the participating agencies to determine the effects of certain variables in the sampling and analytical techniques upon the results obtained. The analytical results normally fall within about one per cent of the true values using standardized nitrate samples and within about five per cent when measuring gaseous samples.[2] It was found that these accuracies can be obtained when standardized and careful techniques are maintained in both the sampling and analytical procedures.

Since combustion processes are variable at least to some degree, even though the rate of fuel feed may be as uniform as is possible to maintain, the results of analyses of grab samples of vented gases will show varying concentrations of the constituents. These variations are more pronounced in the cases of those constituents occurring in the smallest concentrations--in the parts-per-million range. In these circumstances, the analytical results must be interpreted with judgment, eliminating from consideration those data which are at extreme variance with the preponderance of information. The taking of a sufficient number of replicate samples simplifies the detection of obviously non-representative individual samples. It has become standard practice in the field testing phase of the project to obtain a minimum of four replicate samples.

COLORIMETERS

One of the initial investigations was made to determine whether the use of different types of colorimeters might account for discrepancies in the NO_x analytical results. Standardized samples of nitrate solutions were analyzed by the standard phenoldisulfonic acid method, using a Coleman Spectrophotometer, a Klett-Summerson Colorimeter and a Beckman Spectrophotometer. The results obtained using all three instruments showed close agreement on values of nitrate concentrations for the same samples.

FILTERS

During source sampling in the field, a glass fiber filter is employed in the sampling line to prevent particulate matter from entering the sampling bulb. To determine whether this filtration has any effect on analytical results, a number of samples were taken, some with and some without the filter. No significant differences were noted. To determine whether the filters remove any compounds containing nitrogen, hydrogen peroxide-sulfuric acid absorbing solution was used to extract the soluble material from the particulate matter which had been collected in a filter. Analysis showed no NO_x present in this material.

MOISTURE

The effect of condensation of moisture in the sampling lines was investigated. The usual practice is to obtain a dry sample by purging the sampling line prior to taking the sample. In this process the gases being sampled are drawn through the line with an air pump until an equilibrium temperature is reached. There are, however, cases when a hand aspirator must be used to draw the sample, and in these cases moisture collects on the walls of the sampling lines. Replicate samples were collected, using both of these techniques. No significant differences were noted in the analytical results.

ABSORPTION AND OXIDATION MECHANISMS

Some of the difficulties encountered in obtaining consistent analytical results gave rise to two hypotheses: (1) that the amount of shaking given the sample bulb might affect the completeness of absorption, and (2) that the concentration of hydrogen peroxide in the absorbing solution might affect the oxidation rate of the nitric oxide and, hence, the final result. Test procedures were devised to check the validity of these hypotheses.

Several tests were made in which a group of bulbs was shaken in the normal manner while a duplicate group was given no shaking except that which was unavoidable due to handling. There were no significant differences in the results of NO_x analyses obtained from these two groups of samples.

To determine whether the concentration of hydrogen peroxide had any effect on the absorption rate, two series of tests were performed. The

first series was run to determine whether any of the hydrogen peroxide was being lost through the evacuation of the bulbs. Equal volumes of standard solutions of peroxide were placed in a group of bulbs. Half of the bulbs in this group were evacuated for one minute and the other half were evacuated for one hour. The resulting hydrogen peroxide concentrations in all the bulbs were found to be identical upon analysis. The second series of tests was run collecting samples over solutions containing varying concentrations of hydrogen peroxide. Three types of test absorbing solutions made up in N/10 H_2SO_4 were used: one containing the normal amount of H_2O_2, one containing half the normal amount of H_2O_2 and one containing no H_2O_2. For the tests in this series, standardized synthetic flue gases were used. These standards were prepared by injecting known amounts of NO into 50-liter flasks containing a mixture of gases made up of 96 per cent nitrogen and 4 per cent oxygen. This synthetic gas mixture contains approximately the same concentration of oxygen that is found in flue gases from power plant boilers. It was found that the concentration of hydrogen peroxide in the absorbing solution had no significant effect on the analytical results.

SAMPLE BULB PREPARATION

In order to determine whether discrepancies might occur because of loss of vacuum in the sampling bulbs, a number of the bulbs were evacuated and allowed to stand for three days. At the end of this period it was found that the maximum loss in vacuum in any of the bulbs was not greater than 2 mm of mercury. It was concluded that the technique of evacuating the bulbs in advance should not cause appreciable error.

Since sampling bulbs used by one of the laboratories were sealed by stopcocks in which silicone grease was used, tests of standardized known samples were made to determine whether the presence or absence of silicone grease inside the bulbs would affect the results of analysis for NO_x. It was found that the presence of the grease had no effect on the accuracy of the analysis.

MINOR CHANGES IN ANALYTICAL TECHNIQUES

The effects of minor changes in analytical techniques and slight deviations from the standard procedures were checked. Some of these minor changes are:

1. Use of beakers instead of casseroles.

2. Use of a hot plate and drying oven instead of a steam bath for evaporating samples to dryness.

3. Addition of 2 ml instead of 1 ml of phenoldisulfonic acid.

Results of the tests made for checking these minor differences in techniques indicated that these changes do not affect the results, provided that care is used to see that the equipment employed is in good condition and thoroughly cleaned with chromic acid solution prior to use.

DISAPPEARANCE OF OXIDES OF NITROGEN ON STANDING

During the course of the investigations of the factors which might affect the accuracy of the results in the determination of NO_x, integrated samples were collected over a period of one hour to compare with grab samples taken at intervals during the hour. The concentrations of NO_x found in the integrated samples were lower than those in the grab samples. This rather unexpected result led to a series of investigations which has not as yet been completed. From preliminary studies of the results of these investigations, however, it appears that NO will react with SO_2 on standing, causing a reduction in the quantity of NO_x present and the formation of SO_3.

Samples of flue gases from a power plant burning natural gas were taken in dry bulbs, which were allowed to stand for varying periods of time up to 24 hours prior to the introduction of absorbing solution for the determination of NO_x. In these bulbs there appeared to be no reduction in the amount of NO_x with respect to time. Another series of flue gas samples was taken in dry bulbs from exhaust gases of a power plant burning fuel oil containing sulfur compounds. These bulbs were also allowed to stand for varying lengths of time prior to the introduction of absorbing solution. In these cases, the NO_x showed a progressive decrease in concentration with time. Similar results were obtained in tests run by the laboratories of the Air Pollution Control District and of the City of Los Angeles Department of Water and Power. In one experiment the concentration decreased after 18 hours to 46 per cent of the original concentration of 420 p.p.m. In another similar experiment, the concentration of NO_x, originally at 450 p.p.m., decreased to 27 per cent of this value in 24 hours.

During the experimentation carried on to learn the mechanism of the disappearance of NO_x, dry bulbs were used to take simultaneously two series of samples of flue gases from an oil-fired boiler. One series

of samples was taken in the normal manner, using glass fiber filters to remove the particulate matter. The other series of samples was not filtered. Absorbing solution was added to both series of sample bulbs after allowing the samples to stand for varying periods of time. In each series there was found a decrease of NO_x with respect to time.

Another set of experiments was run in which the flue gases were drawn through sodium carbonate solution to remove SO_2 prior to collecting the gas in dry bulbs. The absorbing solution was then added after allowing the samples to stand for varying periods of time, as before. In these experiments, no reduction of NO_x with time was observed. Experiments including time intervals beyond 24 hours have not yet been run.

Thus, preliminary experiments appear to suggest that in flue gas samples contained in dry sample bulbs, SO_2 tends to reduce the amount of NO_x, at least at the concentrations encountered. This observation has been considered to be of sufficient interest to warrant laboratory investigations of the mechanism of this reaction using gaseous mixtures with known amounts of pure components such as SO_2, NO and NO_2. The results of these investigations will be described in a future report.

IV. SMALL SOURCES OF NO_x

The number of actual units in the small-source category precluded the testing of more than a few units of each type. The number of tests made on any given type of equipment varied according to the relative importance attached to the NO_X contribution by that type as compared to the total production of NO_X by all the small sources. In instances where only a few units exist, it was deemed necessary to test at least one unit. In other cases, only a relatively small percentage of all similar units could be tested.

In determining the census data for various units of equipment, several sources of information were used. It is believed that the most reliable data are those provided by the Southern California Gas Company (concerning the count of domestic and commercial appliances) and those where other actual counts were made. Fortunately, the census data which were the results of estimates and calculations are for the units which are the least significant in terms of total NO_X production.

The emission and usage factors are the results of evaluation of the test data and usage information gathered. It should be realized that each individual piece of equipment will differ from all others with respect to operating conditions, adjustment, load factor, operating temperature, etc. All these factors influence the rate of production of NO_X. Usage factors in some cases reflect only an order-of-magnitude estimate, while in other cases the usage factors may be determined quite accurately. Usage factors based on production figures are generally estimates provided by the various industries and may or may not give a true picture at the present time. Changing business conditions can have profound and rapid effects on usage factors. In each case, every effort was made to calculate an emission factor and a usage factor which would represent average conditions.

The sources evaluated represent most of the common types of equipment which constitute the small-source category with respect to NO_X production. Obviously, not all types of existing equipment could be tested in the time allotted. It is felt, however, that the sources evaluated represent the preponderance of the units of stationary equipment which produce less than five pounds per hour of NO_X. The results of this evaluation may, therefore, be slightly on the low side rather than on the high side, but only to the degree that the project may have failed to include a few types of sources.

Details of analytical and other test data are shown in Tables VI and VII for gas-fired space heaters and for electric-arc furnaces used for steel melting. The procedures and bases indicated in these tables for calculating NO_x discharge are typical of those used in calculating NO_x emissions from all small sources. In the interest of brevity, similar details will be omitted for the remainder of the tests included in this report. Ranges of NO_x concentrations found, however, are shown in Table I for all types of equipment.

FUELS USED IN LOS ANGELES COUNTY

Since the production of oxides of nitrogen is associated primarily with high temperature processes or with chemical processes involving compounds containing nitrogen,[1] the study of fuel sources was a logical starting point. High temperature processes other than combustion of common fuels include welding operations, incineration and operations involving electrical discharges. All such processes are represented in this study.

The major fuel used in Los Angeles County is natural gas. For equipment in the small source category it is nearly the exclusive fuel used. Since all reports in this series will be based on projected NO_x production at the end of 1960, it is necessary to look a short distance into the future for a common basis for all data. Table II shows the proportions of domestic and non-domestic gas consumers and their relative gas requirements.

TABLE II

ESTIMATED NUMBER OF NATURAL GAS CUSTOMERS
AND GAS CONSUMPTION IN
LOS ANGELES COUNTY DURING 1958[3]

Type of Customer	No. of Customers	Per Cent of Total Customers	Total Consumption Millions of Cu. Ft.	Per Cent of Total Gas Consumption
Domestic	1,737,000	90.8	125,117.8	39.6
Firm Non-Residential	174,591	9.1	46,822.0	14.8
Interruptible Non-Residential	958	Less Than 0.1	59,406.0	18.8
Electric Generation	5		83,754.0	26.5
Gas Engine	169*		960.0	0.3
TOTALS	1,912,723	100.0	316,059.8	100.0

* Estimated number of customers with gas engines only served from the meter.

Figure 1 shows the increase in domestic consumers of natural gas in Los Angeles County since 1950.[3] It was found by extrapolating the curve that 1,900,000 domestic gas consumers can be anticipated by the end of 1960. Since the data used for calculations were those estimated for the end of 1958 (1,737,000 consumers), the gas consumption rate at the end of 1960 can be assumed to be in direct ratio. All data reported in Table I regarding NO_x production based on 1958 natural gas consumption, therefore, have been multiplied by the factor 1.095. The year 1958 was chosen as the basis for calculations since it is the latest full calendar year for which complete data from the gas distributors are available in the form needed for the calculations to be performed for this project.

The variations in the rate of natural gas consumption in Los Angeles County for the year 1958 are shown in Figure 2, plotted on the basis of monthly usage. "Domestic" gas consumption includes all residential uses, single or multiple dwelling. "Industrial" gas is that consumed by the manufacturing industries. "Commercial" includes all other business gas requirements.

In Los Angeles County gas-fired equipment may be found in all categories of use--domestic, commercial and industrial (including oil refining and power generating). All domestic and most commercial gas is sold on a firm basis.* Some industrial users purchase firm gas but most of the larger users are provided only interruptible service. Power generating plants all receive only interruptible service. Industrial and commercial uses of firm gas supplies are much less variable than are domestic uses. Monthly domestic consumption as shown in Figure 2 was calculated by taking the difference between all firm gas sold and that used by firm commercial and industrial consumers. The preponderant and almost the only variation in domestic gas consumption is that caused by space heating requirements. Since space heating in Los Angeles County is almost entirely confined to the six months' period beginning with November and ending with April, the amount of domestic gas used during the remainder of the year can be considered to be essentially the basic

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* "Firm" gas supplies may not be cut off by the gas distributor, barring a catastrophe. "Interruptible" gas supplies may be curtailed by the distributor when "firm" gas demands increase beyond normal requirements, e.g., during periods of unusually cold weather. For curtailment schedules see Table X.

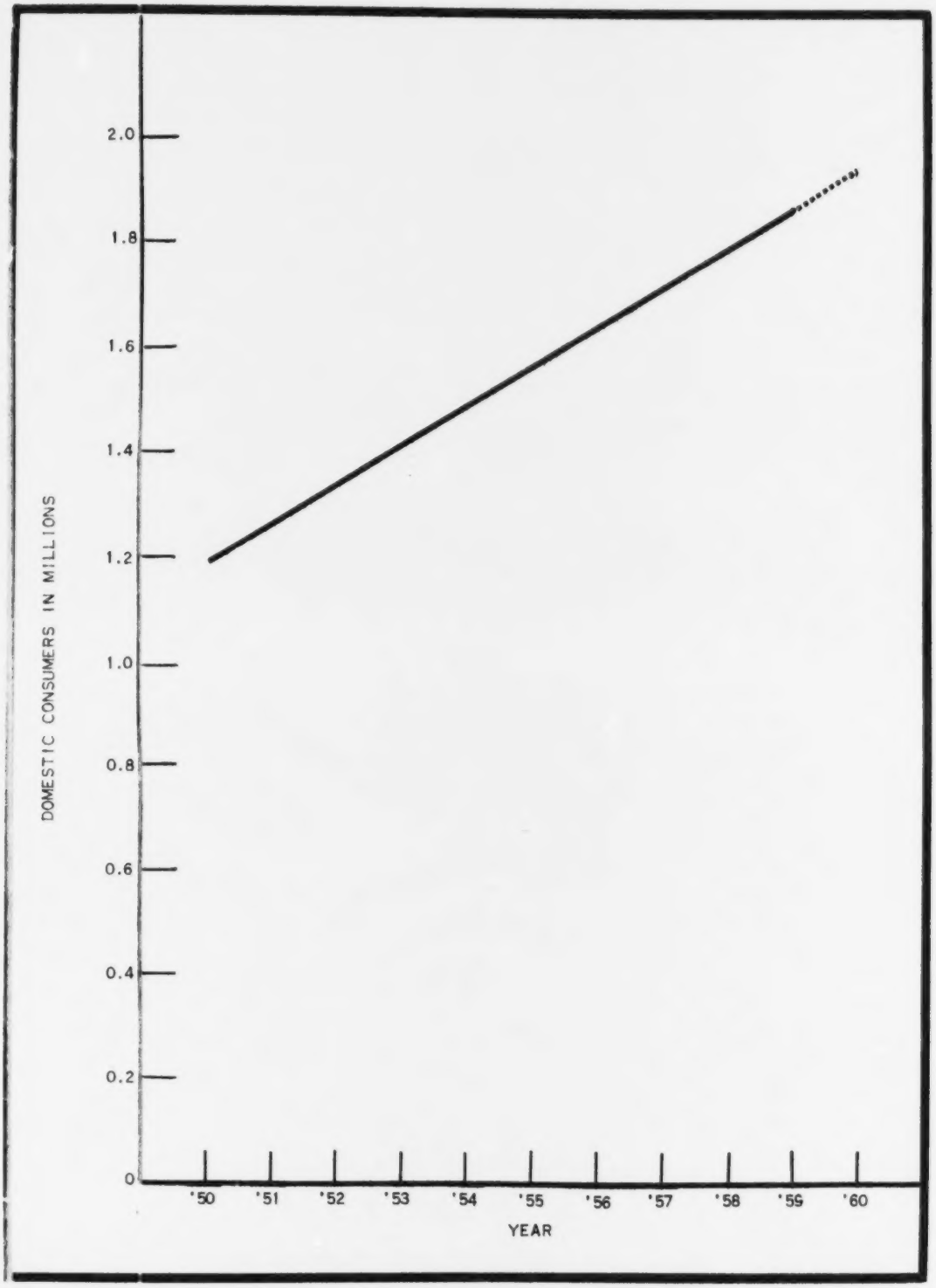

Figure 1. The number of domestic consumers of natural gas in Los Angeles County increased steadily during the period 1950 to 1959.

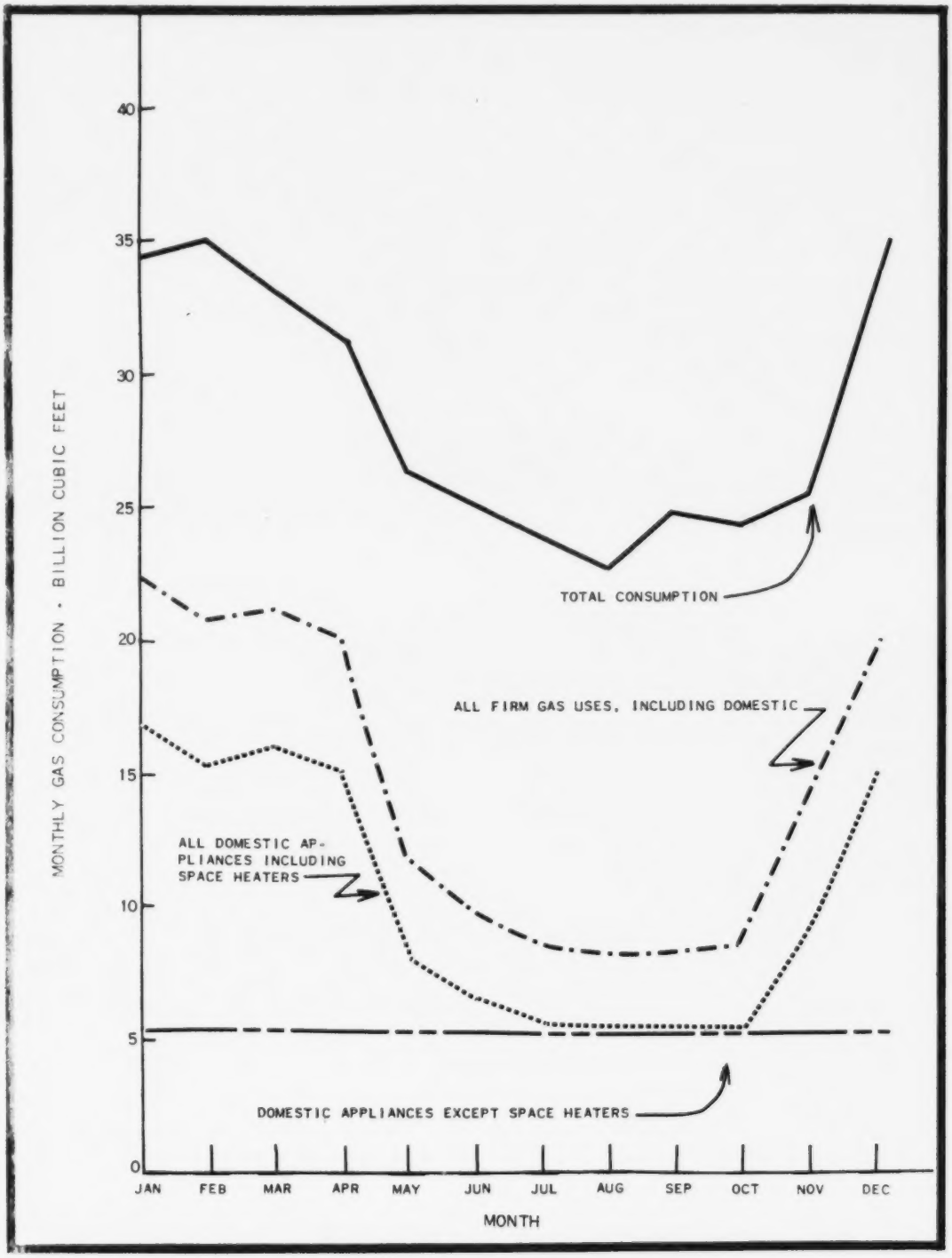

Figure 2. Natural gas consumption in Los Angeles County during 1958 shows the effect of decreased demand for space heating during the summer.

amount required for cooking, water heating, refrigeration, drying of clothes and miscellaneous uses. In Table I, the period from November to April, inclusive, is referred to as "winter," and the remainder of the year is labeled "summer." Figure 2 shows the effect of reduced domestic gas requirements during "summer" upon total gas consumption.

Natural gas, which is piped into the Los Angeles area from Texas, passes through natural gasoline absorption plants. The extraction of butane and propane is better during the cooler months of the year. Thus, natural gas will contain more butane and propane in the summer than in winter, affecting the gas heating value to a small degree. The variations in the heating values of natural gas available in the Los Angeles area during 1959 are given in Table III.

TABLE III

HEATING VALUE OF NATURAL GAS IN LOS ANGELES COUNTY DURING 1959[4]

Month	Btu per Standard Cubic Foot	Month	Btu per Standard Cubic Foot
January	1084	July	1093
February	1083	August	1095
March	1086	September	1096
April	1088	October	1091
May	1090	November	1090
June	1093	December	1084

Calculations made for this report are based on a natural gas heating value of 1090 Btu per standard cubic foot, since this figure represents a good average and since the variations in heating value have a negligible effect on the final data.

DOMESTIC AND COMMERCIAL GAS APPLIANCES

All of the equipment to be discussed in this section is used primarily to provide a source of heat for such operations as cooking, baking, heating water, drying clothes, refrigerating or providing heat for bodily comfort in buildings. Each individual unit of equipment in this group is a relatively small user of gaseous fuel by itself. However, these types of appliances are used in such large numbers that the total emission of NO_x from this group becomes the most significant in the entire small-source category. This equipment is nearly always fired with natural gas, and provisions for oil standby are made only for some relatively large commercial installations. Gas-fired commercial equipment includes ranges, friers, broilers, griddles, space heaters, clothes driers and water heaters.

The projected estimates for equipment census data and for gas consumption by domestic and commercial gas-fired equipment are shown in Tables IV and V. These data have been calculated from 1958 gas consumption figures[5] corrected for population increase up to the end of 1960.

TABLE IV

ANNUAL RATE OF GAS CONSUMPTION BY DOMESTIC GAS-FIRED EQUIPMENT IN LOS ANGELES COUNTY, BY THE END OF 1960[3]

Equipment	Number Pieces of Equipment at End of 1960	Gas Consumption Millions of Cu. Ft. Per Year	Gas Heating Value, Billions of Btu Per Year
Space heaters	1,900,000	69,400	75,500
Water heaters	1,848,000	43,000	46,900
Ranges	1,727,000	21,300	23,200
Refrigerators	199,000	1,900	2,070
Clothes driers	144,000	533	581
Miscellaneous*	14,200	710	725

* Gas air conditioners; gas logs; portable room heaters; etc.

TABLE V

ANNUAL RATE OF GAS CONSUMPTION BY COMMERCIAL GAS-FIRED EQUIPMENT IN LOS ANGELES COUNTY, BY THE END OF 1960[3]

Equipment	Number Pieces of Equipment at End of 1960	Gas Consumption Millions of Cu. Ft. Per Year	Gas Heating Value, Billions of Btu Per Year
Space heaters	371,000	9,620	10,500
Water heaters	186,000	5,125	5,580
Ranges	19,600	4,330	4,720
Griddles	6,800	890	970
Broilers	6,350	616	672
Friers	5,470	415	452
Clothes driers	4,520	3,750	4,100

SPACE HEATERS

Although some large buildings are heated by the use of steam or hot water radiators, by far most of the space heating in Los Angeles County is accomplished by the use of gas-fired hot air furnaces of one type or another. Of the several types of these space heaters in use the two most common are the wall-type and the forced-air type. Examples of these heaters are shown in Figures 3 and 4.

From the data describing domestic and commercial gas consumption, Tables IV and V and Figure 2, it can be seen that the bulk of the natural gas used for space heating is consumed during the six months' period beginning in November and continuing through April. This gas used for space heating comprises approximately half of all domestic and commercial gas consumption over a year's time as well as over 40 per cent of the entire year's firm gas consumption.

Tests of seven space heaters showed an average concentration of 48 p.p.m. of NO_x, as shown in Table VI. From the volumes of the vent gases, it was calculated that these units discharge an average of 0.093 pound of NO_x per million Btu. From gas consumption data it was calculated that the average usage factor for such units is 2.3 hours per calendar day during the heating season and essentially zero hours per day during the remainder of the year.

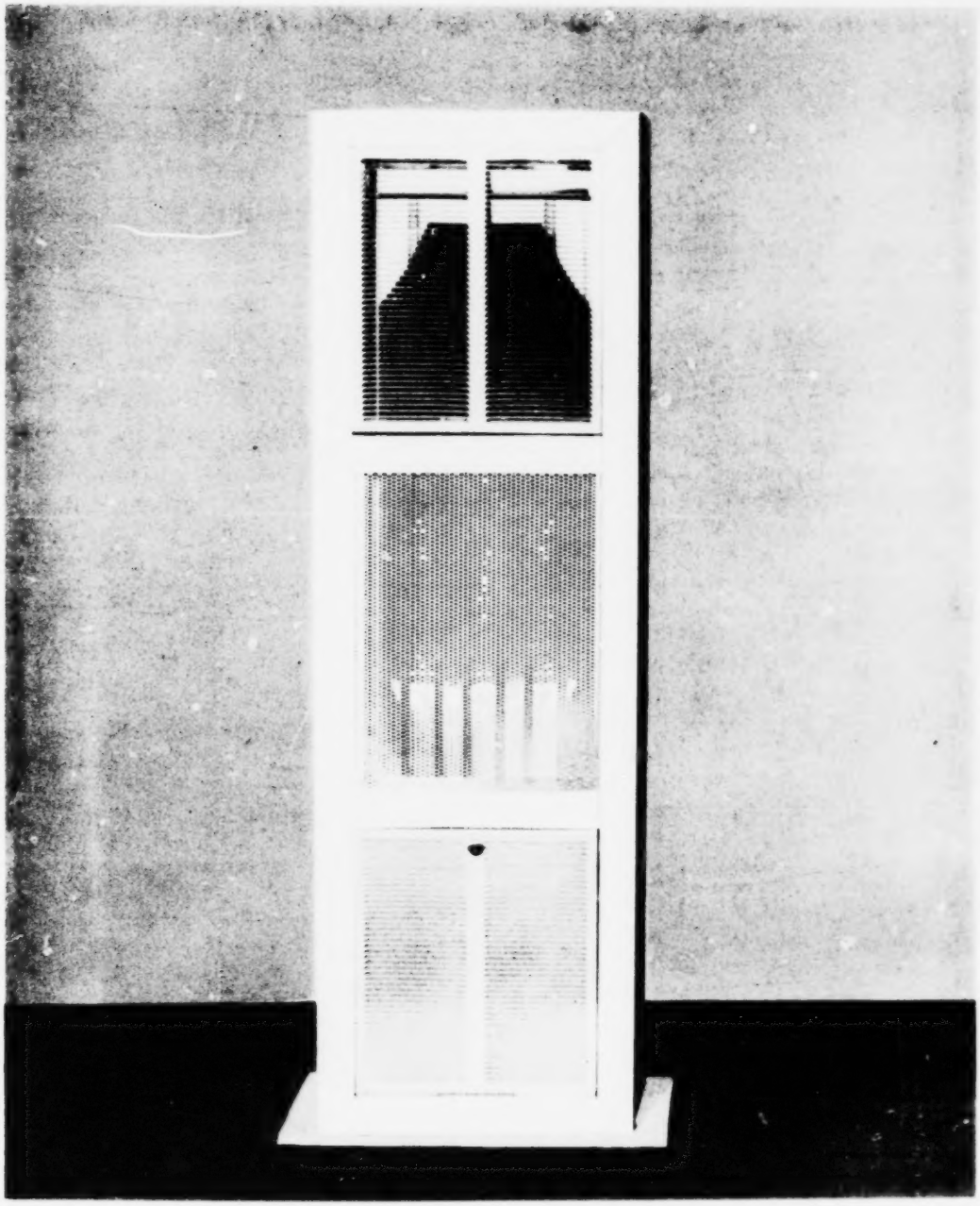

Figure 3. Wall-type space heaters rated at 20,000 to 40,000 Btu/hour are commonly used in small homes and apartments in Southern California.

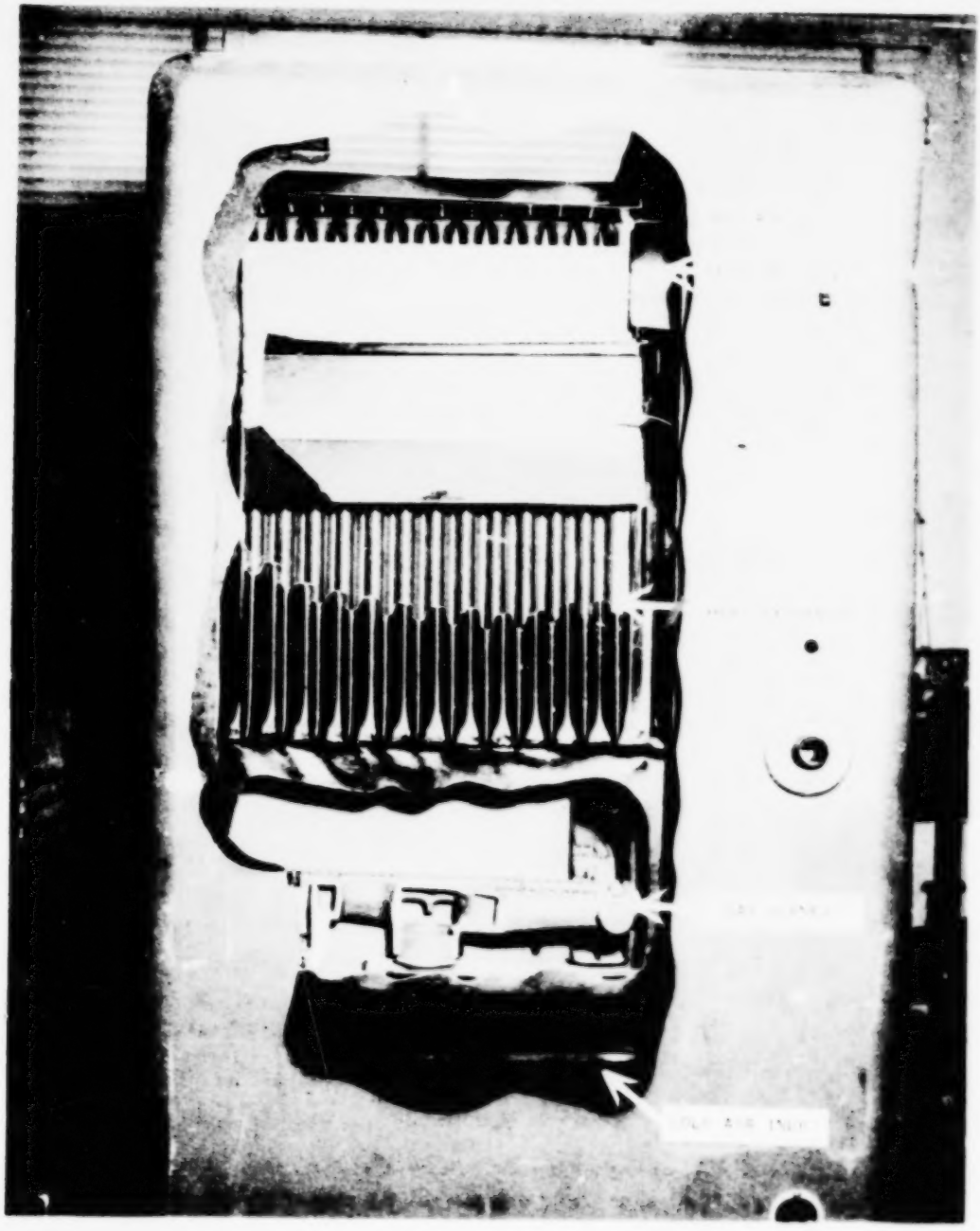

Figure 4. This cut-away view of a forced-air type residential space heater shows the paths of the combustion gases and the heated air.

Space heaters contribute approximately 22 of the 38 tons per day of NO_x produced by all gas appliances, domestic and commercial, during the winter months. During the summer months space heaters produce essentially no NO_x. Details are shown in Table I. Although a daily average of 11 tons of NO_x from these units is reported for the year, this figure is only technically an average, considering the circumstances.

OTHER DOMESTIC AND COMMERCIAL APPLIANCES

Domestic and commercial appliances other than space heaters utilize gas at a rate which is affected but little by the seasons, as is shown in Figure 2.

A total of 17 tests were performed to determine the rate of NO_x production by these units. Figure 5 shows the hood used for collecting the samples from the top burners on a gas range. In other instances similar means were used to collect the products of combustion for sampling, or the samples were taken in the stack or vent.

It was found that as a group these appliances produce 16 tons per day of NO_x. Details are reported in Table I. Figure 6 shows the effect of seasonal variations in gas consumption on NO_x production by all domestic and commercial gas-fired appliances.

TABLE VI

RESULTS OF TESTS OF NO_x EMISSIONS FROM VARIOUS SIZED GAS-FIRED SPACE HEATERS

Type of Space Heater	Btu Per Hour Rating	Btu Per Hour Actual Consumption	Exhaust Gas Volume, SCFM	Concentration of NO_x in Vented Gases, P.P.M.		Average NO_x Discharge Lb/Hr	Average NO_x Discharge Lb/10^6 Btu
				Analytical Results from Replicate Samples	Avg.		
Wall-type	30,000	35,200	8.44	51.4, 51.2, 51.0, 48.4	50	0.0031	0.088
Forced air	150,000	128,500	81	19.9, 16.3, 20.0, 15.7	18	0.016	0.13
Wall-type	20,000	22,500	5.03	43, 44, 49, 48.5	46	0.0017	0.075
Forced air	75,000	80,200	22.3	46.8, 48.5, 40.0, 44.8	44	0.0072	0.089
Forced air	190,000	186,000	43.8	62.0, 64.4, 54.0, 64.2, 73.3, 70.5, 72.1, 73.0	62	0.020	0.11
Natural draft	80,000	85,700	17.1	54.8, 64.7, 66.7, 59.5, 63.7	62	0.0077	0.090
Natural draft	80,000	80,000	14.6	58.9, 61.5, 58.4, 51.2, 49.3, 47.0, 49.2, 47.1	53	0.0056	0.070
Average (All classes)					48	0.0087	0.093

Figure 5. The testing of surface burners of gas ranges was done using a hood. A water filled pot was used to provide a load and was vented separately from the combustion gases.

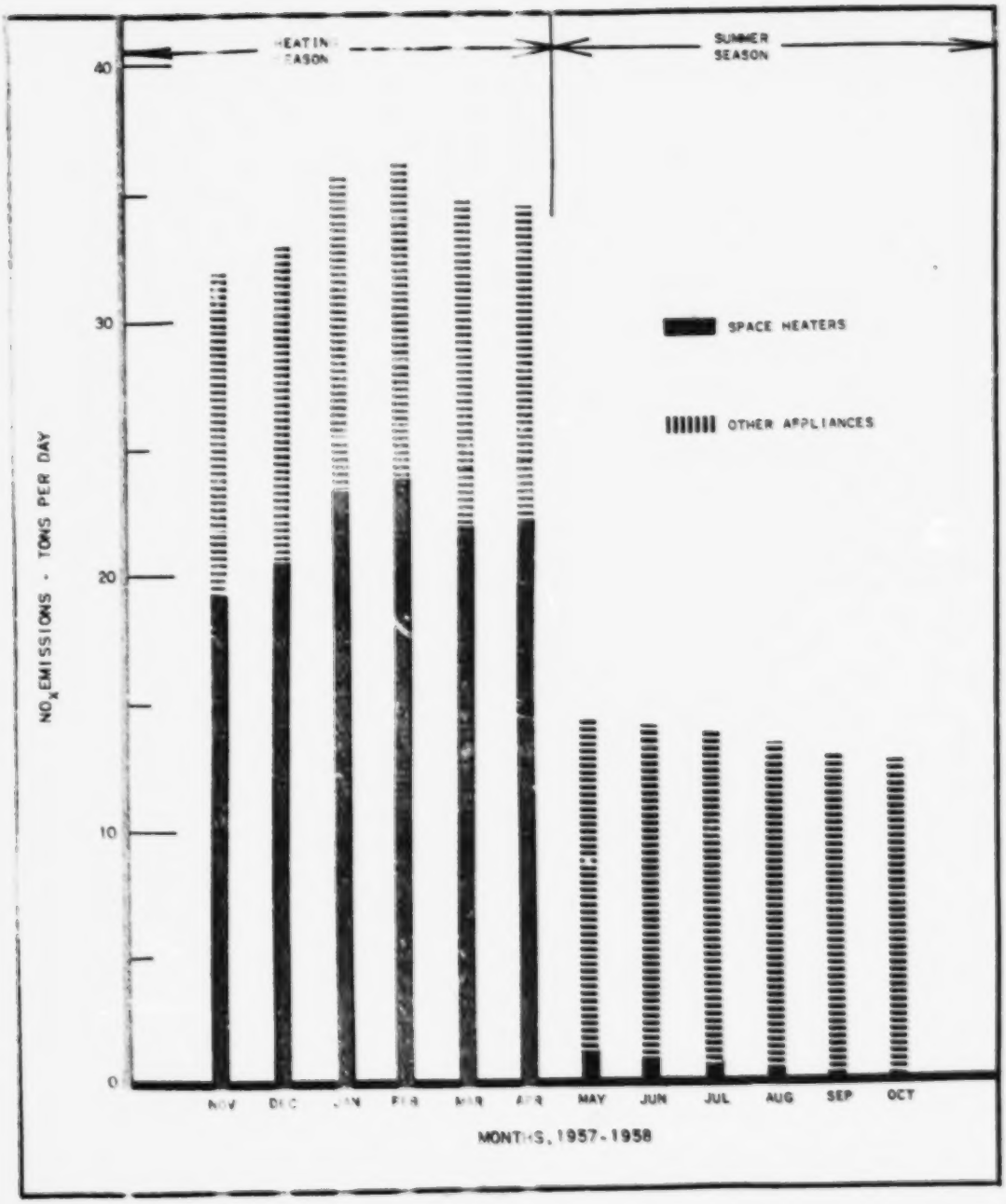

Figure 6. The amount of NO_x emitted by domestic appliances varies with the seasonal changes in gas burned to meet space heating requirements.

METALLURGICAL FURNACES

Metallurgical furnaces in the small-source category used in Los Angeles County, including those used for ferrous and non-ferrous operations, produce an average of 1300 pounds per day of NO_X. This grouping comprises primarily the metal-melting furnaces: crucible, reverberatory, induction and sweat furnaces for non-ferrous operations; direct arc, induction, reverberatory and cupola furnaces for steel and secondary iron-melting operations. Heat-treat furnaces and steel mill "soaking pits" were included with this group mainly for convenience in classification. The censuses of these units consist of actual counts from Los Angeles County Air Pollution Control District records. Typical furnaces and typical metals of each class were chosen for testing for NO_X production. Test results are shown in Table I.

Data taken during two of the series of tests were the subjects of special studies to determine if there were any correlations between the NO_X production and the types of metals being melted in a given type of furnace or between the NO_X production and the size of the furnace in which a given type of metal was being melted. These studies cover the discharge of NO_X from:

1. Gas-fired, crucible-type and pot-type furnaces, where the variable was the type of metal melted.

2. Coke-fired, cupola-type furnaces melting gray iron, where the variable was the cupola diameter (which, in turn, is a rough measure of the average melting rate and the amount of fuel consumed per unit time).

It was found that in the crucible furnaces used for melting non-ferrous metals, the concentrations of NO_X in the vented gases were roughly proportional to the range of temperatures at which the particular metal concerned was heated, as is shown in Figure 7. It should be pointed out, however, that in order to obtain the degree of heat required to melt the metals with the higher pouring temperatures, it is necessary to supply proportionately more fuel in the same size of furnace. Since up to the maximum attainable temperature the variations in the temperatures in a given furnace are proportional to the volumetric rate of heat release in the firebox and therefore to the rate of fuel input, these data were re-examined on the basis of weight of NO_X produced per million Btu heat input to the furnace. It was found that on that basis the weights of NO_X

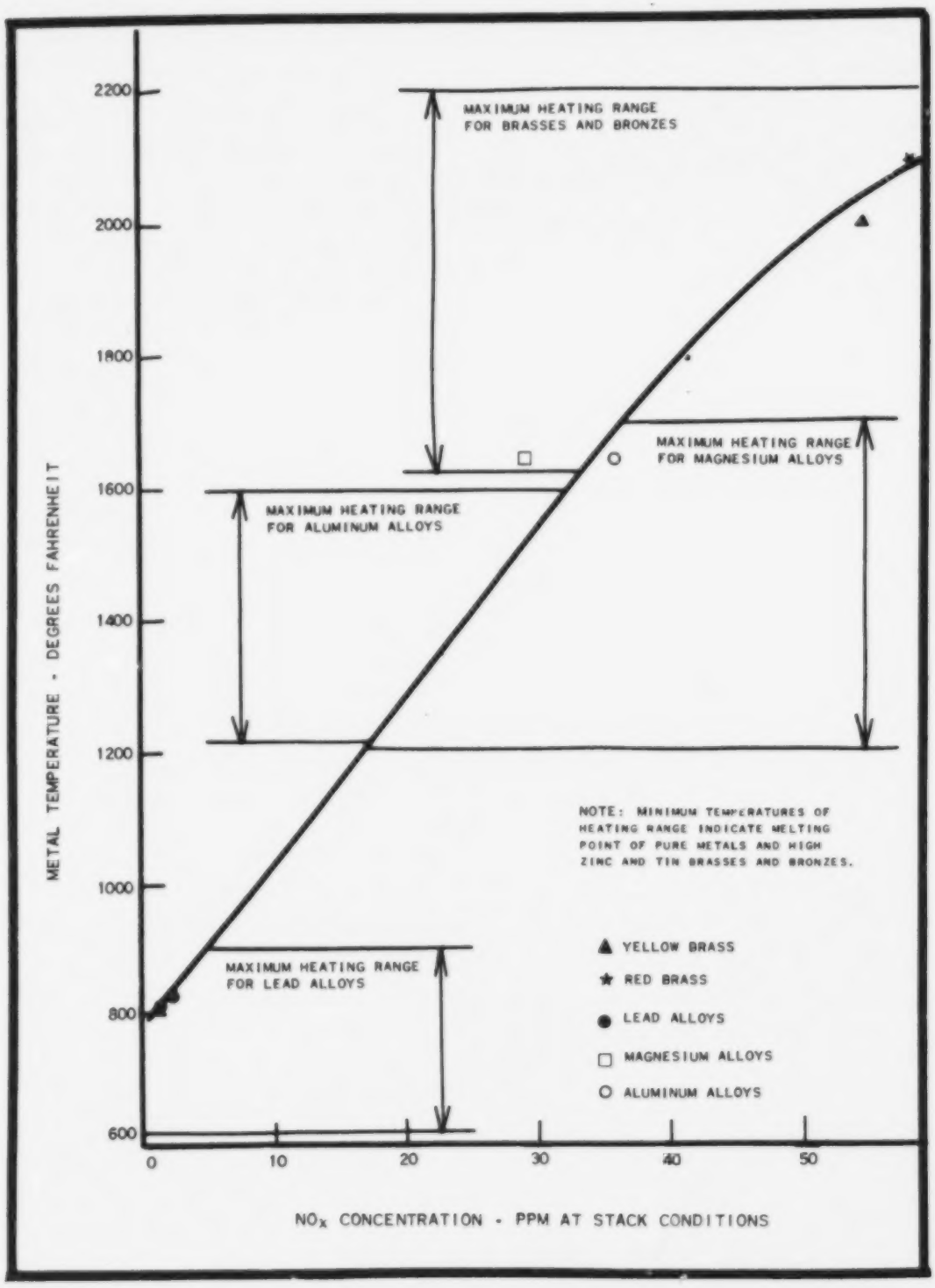

Figure 7. The concentration of NO_x in vent gases from crucible-type metal-melting furnaces varies with the furnace temperature required.

produced in crucible-type furnaces were much more nearly constant, as is shown in Table I, varying between 0.040 and 0.071 pound per million Btu. These results suggest the hypothesis that the total amount of NO_X produced may be proportional to the total amount of heat or fuel supplied, while the concentration of NO_X in the vent gases may be proportional to the temperature in the furnace.

In the studies of the cupola furnaces used to melt gray iron, it was found that the amount of NO_X produced per hour increased in proportion to the size of the cupola (and, correspondingly, to the amount of coke burned), as is shown in Figure 8. On the other hand, the weight of NO_X produced on a metal-production basis varied but little, as is brought out under the discussion of cupolas, remaining very close to 0.11 pound of NO_X per ton of metal melted. The data gathered during this series of studies, too, support the hypothesis that the amount of NO_X produced is more nearly proportional to the amount of fuel consumed than to the furnace temperature. For these reasons, the calculation of the daily NO_X production from cupola furnaces was based on tons of metal melted.

ELECTRIC ARC FURNACES

Electric arc furnaces for melting iron and steel in Los Angeles County are usually of the direct-arc types, i.e., those in which the electrodes extend into the charge. In the direct-arc furnace, many small arcs burn between the electrodes and the various pieces of metal in the charge. These multiple arcs produce many small high temperature zones and were originally believed to be capable of bringing this type of furnace into the medium source class. Test results, which are summarized in Table I, show not only that these direct-arc furnaces are small sources but also that the metal-holding capacity of the furnace has little or no bearing on the rate of NO_X production.

There are twenty-three direct-arc furnaces used for steel melting in Los Angeles County. At the present time there are sixteen of these furnaces in operation for approximately 900 furnace-hours per calendar week (an average of 8.0 hours per furnace per calendar day). It is estimated that by the end of 1960, considering the expected upturn in business, that production will require a total of 1640 furnace-hours per week (an average of 10.2 hours per furnace per calendar day for 23 furnaces or 14.6 hours per furnace per calendar day for 16 furnaces).

Large (75-ton capacity) and small (2-ton capacity) direct-arc furnaces were investigated for NO_X emissions. The exhaust volumes measured

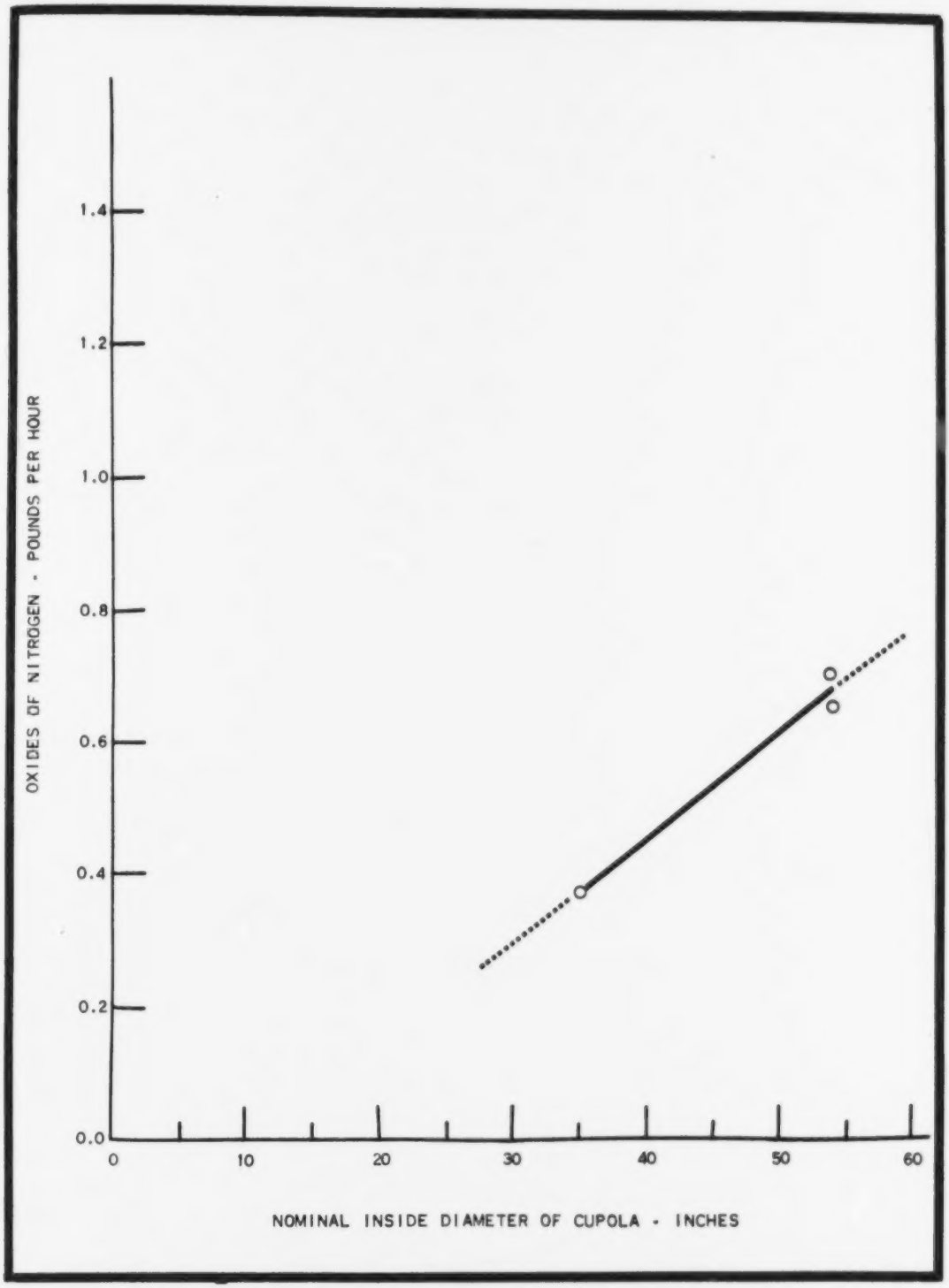

Figure 8. The emission rate of oxides of nitrogen from gray iron cupolas varies with the size of the cupola for a given iron-to-coke ratio.

from these furnaces do not represent the actual volumes of the gases normally vented from such furnaces. The volumes of the exhaust gases are much higher than would be expected, since all such furnaces are connected to local exhaust systems venting to air pollution control devices; the high exhaust volumes are required to insure complete pickup of the fumes from the furnaces. As a result of this dilution, the NO_x concentrations measured are lower than those which would be found in the normal volume of arc-furnace vent gases. Details of the test results appear in Table VII.

In one plant, a 75-ton furnace (nominal capacity) was tested on two occasions, with different operating conditions occurring within the test periods, such as during the starting surge of a heat, during the melt-down, during a heat-holding period, at the end of a heat and with a similarly-sized unit being used at the same time and venting through the same exhaust system.

The exhaust gas volumes reported in Table VII are the averages of the measurements made during the test period. The draft on this furnace is automatically controlled, and the exhaust gas volume is continuously metered. The overall average rate of NO_x discharge was calculated from the average of values obtained by analysis of the grab samples.

In another plant, two 2-ton furnaces (nominal capacity) were tested to determine the range of values of NO_x emissions between the largest and smallest electric-arc furnaces in the County. The test results were surprising in that they showed little or no difference in NO_x production between the 75-ton and the 2-ton furnaces. It was concluded that the size of the furnace is not a measure of the NO_x-producing capability. Since it is known that NO_x is formed in electric arcs, it seems probable that the amount formed is a function of the degree of arcing during the heating.

The total NO_x emissions from direct-arc furnaces average 2.4 pounds per hour per furnace. Based on 1640 furnace-hours per week, the total NO_x production will amount to 562 pounds (0.28 ton) per calendar day at the end of 1960.

TABLE VII

NO_x PRODUCTION IN ELECTRIC-ARC STEEL-MELTING FURNACES

Test No.	Furnace Data	Average Exhaust Gas Volume SCFM	Average Exhaust Gas Temp. °F	NO_x Concentration in Vented Gases P.P.M.[a]		NO_x Emission Per Furnace Lbs/Hr
				Results of Replicate Samples	Average	
1	1 75-ton furnace	22,000	145	25, 15, 29, 20	22	3.5
		75,000	130	7.6, 8.4, 11, 2.7	7.4	4.1
2	2 75-ton furnaces (206,000 lbs metal in #1) (204,000 lbs metal in #2)	72,600	160	5.2, 5.0, 17[b], 5.9	5.4	1.4
	1 75-ton furnace (Furnace #2 only)	35,800	155	3.9, 1.8, 3.3 3.0	3.0	0.74
3	2 2-ton furnaces (8552 lbs metal in #1) (8401 lbs metal in #2)	14,400	140	15, 53, 25, 38, 54, 36, 45, 54, 57, 52, 75, 77, 35, 48, 31	46	2.4

[a] At stack conditions

[b] Not used in average

CRUCIBLE AND POT-TYPE FURNACES

Crucible furnaces in Los Angeles County are used primarily for melting brasses, bronzes, aluminum and magnesium. Figure 9 shows a representative furnace of the tilting-crucible type. Figure 10 shows a sectional view of this type of furnace, in which it can be seen that the crucible holding the metal is completely surrounded by the firebox or combustion space, except at the bottom. Temperatures are regulated by controlling the rate of fuel input. Since magnesium is highly combustible, crucible furnaces to be used for melting magnesium are modified slightly so that the surface of the metal in the crucible cannot come in contact with the flames. Products of combustion are vented from a side stack instead of from the top of the furnace. For lead, the crucible is usually replaced by a metal pot suspended from the top of the furnace, with the products of combustion venting separately in a manner similar to that employed for magnesium crucibles. Temperatures in the fireboxes vary over the melting period, depending on the rate of heating and the particular metal being melted. The usual fuel is gas, since amounts required are relatively small and since regulation is simple.

Seven tests were made to measure the NO_x in the stack gases from furnaces melting aluminum, brass, bronze, lead and magnesium. A summary of the results of the tests is reported in Table I. There are over 900 furnaces of these types in Los Angeles County. The total NO_x contribution of the entire group is calculated to be 0.13 ton per day.

REVERBERATORY FURNACES

In Los Angeles County reverberatory furnaces are used for both ferrous and non-ferrous metals. The large reverberatory furnaces used for steel-melting have been found to be "medium sources," producing over five pounds of NO_x per hour, and will be included in a subsequent report. Small reverberatory furnaces are used mainly for non-ferrous metals--aluminum, brasses, bronzes, lead and zinc. In recent years reverberatory furnaces of from 500 to 4000 pounds capacity have also been used as replacements for cupola furnaces for melting gray iron in small, job-shop foundries as well as in other foundries where mold-pouring can be scheduled on a more-or-less continuous basis during the day.

Seven tests were run to determine the amounts of NO_x vented from the 125 furnaces of this type in operation in the County. This group of equipment produces only 0.12 ton per day of NO_x. Table I summarizes the data taken on these units.

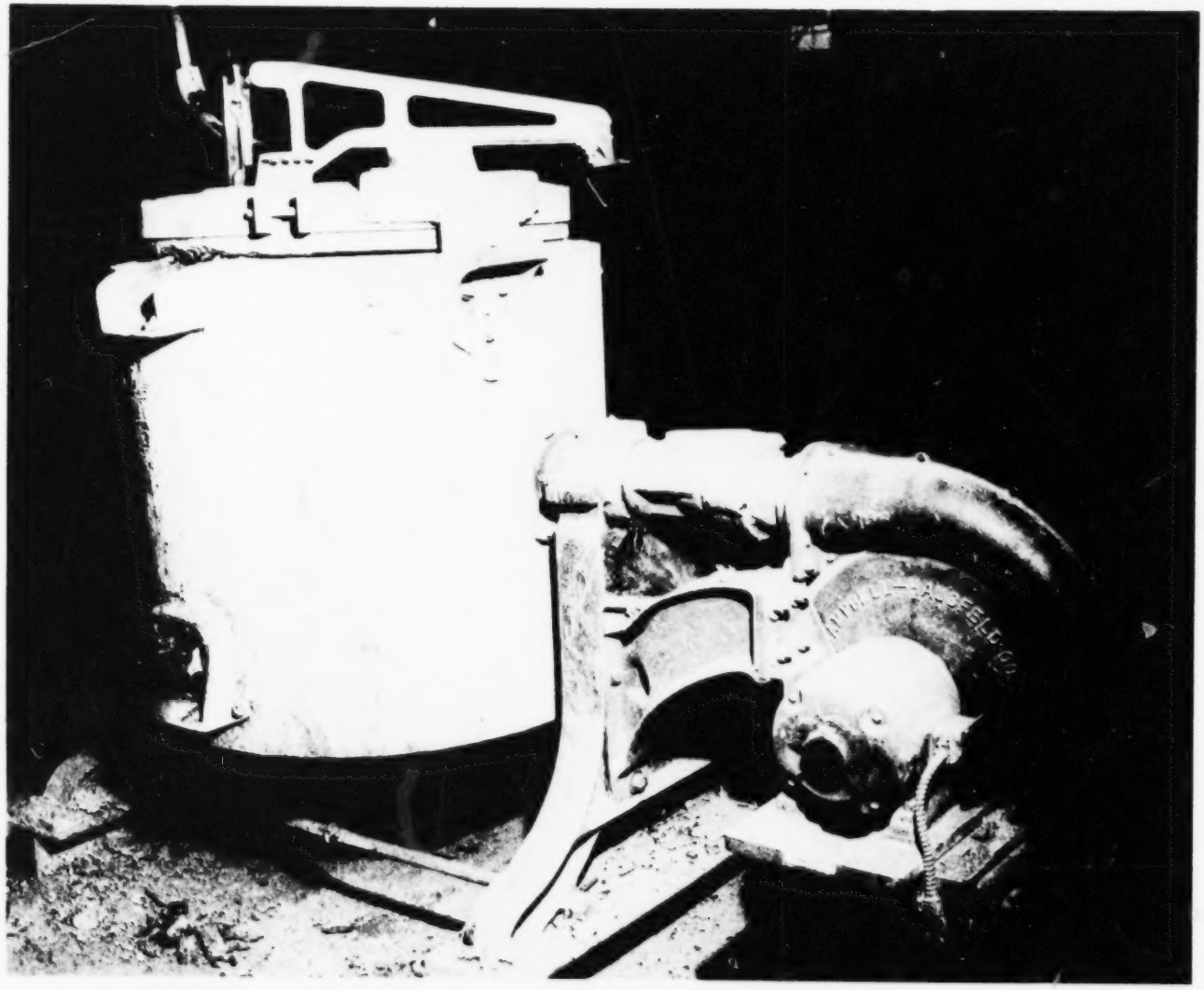

Figure 9. This picture shows a crucible-type metal-melting furnace for brass. During operation flames project from the two side ports as well as from the center of the lid.

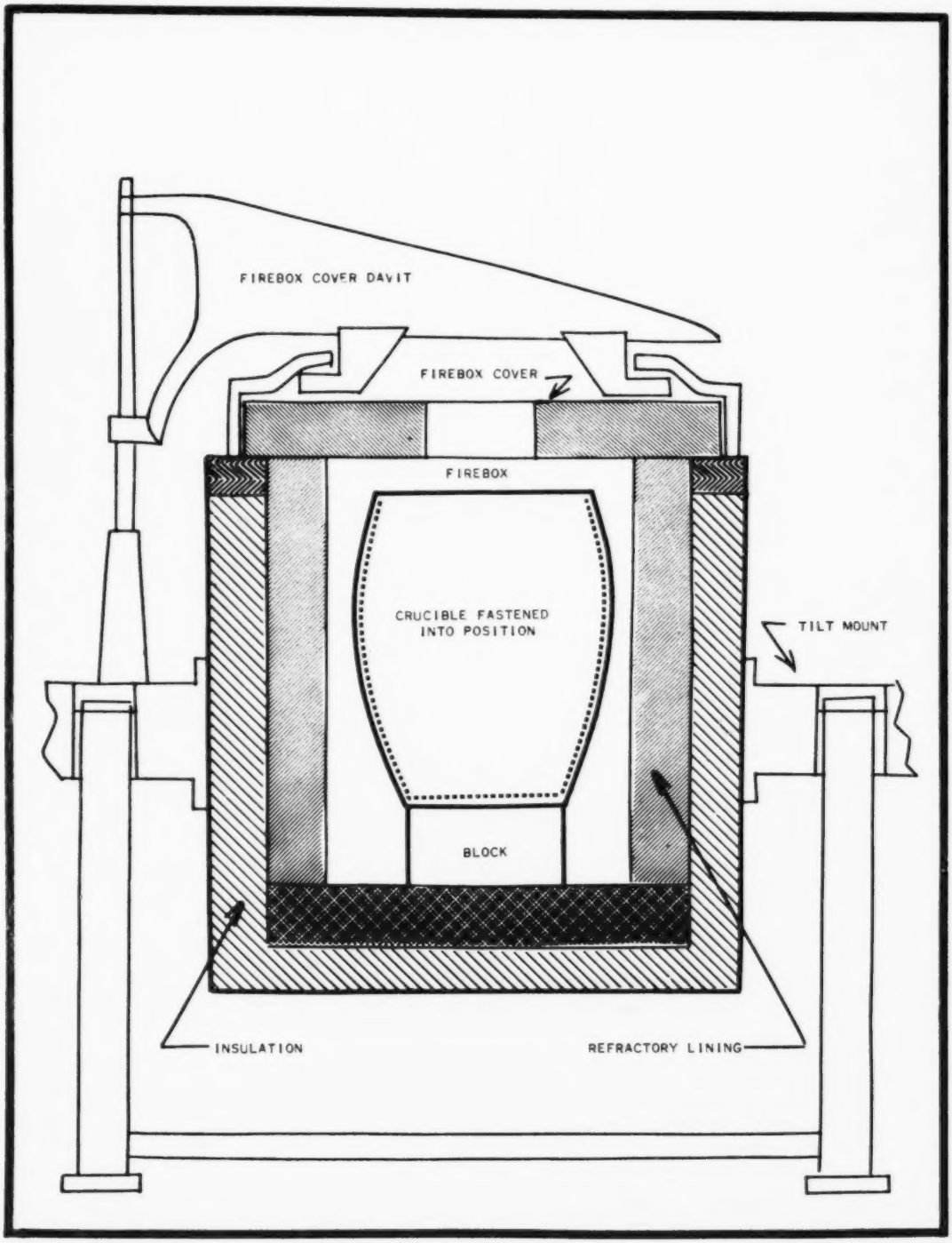

Figure 10. This vertical-sectional view shows the general interior construction of the crucible-type metal-melting furnace shown in Figure 9.

SWEAT FURNACES

Sweat furnaces can be classified as reclaiming furnaces, since the process is that of melting one metal or alloy away from scrap which includes one or more other metals or alloys which possess higher melting temperatures. Many of these furnaces are crudely built, such as that shown in Figure 11. These units ordinarily operate at a much lower average temperature than the usual metal-melting furnace.

There are 49 furnaces of this type in the County. These units produce a total of only 0.02 ton of NO_x per day. Results of analyses are summarized in Table I.

GRAY IRON CUPOLAS

As was mentioned in the general discussion of metallurgical furnaces, gray iron cupola furnaces were chosen for special studies to determine whether or not the size of furnace had any bearing on the rate of NO_x production while melting a single kind of metal.

Cupolas in Los Angeles County are used to produce gray or white-iron castings. Various sizes are employed, with the smallest being 23 inches nominal inside diameter and the largest 63 inches. The latest census of these units in the County showed that 44 cupolas were in operation, producing 518 tons of cast metal per calendar day. Normal daily durations of furnace operation are quite variable; some cupolas are run as few as three hours per working day and some as many as 16 hours. The cupolas chosen for testing utilized a uniform iron-to-coke ratio, thus eliminating any possible variations which might be ascribed to different combustion characteristics. The total discharge from all cupolas was found to be small enough so that differences ascribable to variations in the iron-to-coke ratio could be neglected.

Table I shows a summary of results of tests of cupolas. Four tests were run, but the results of one test were discarded because of wide and unexplainable variations in values obtained. The data from the three good tests are shown in Table VIII. These values were used to produce the graph shown in Figure 8. Although the total amount of NO_x is greater from the larger furnaces, the amount of NO_x produced on a basis of pounds per ton of metal melted remains almost the same regardless of the size of the cupola. The actual concentrations of NO_x in the vent gases also remain nearly constant. This phenomenon is understandable since the volume of vent gases is directly proportional to the rate of metal-melting as long as the iron-to-coke ratio is kept constant.

Figure 11. The sweat furnace shown here is used to reclaim zinc from other metals. Scrap metal is placed on the exterior hearth and manually pushed into the furnace.

TABLE VIII

NO_x EMISSIONS FROM GRAY IRON CUPOLAS

Test No.	Tons/Hr of Metal Produced	Oxides of Nitrogen Emissions		
		Concentration in Vent Gases P.P.M.	Pounds Per Hour	Lbs/Ton of Metal Produced
1	2.50	20	0.38	0.15
2	6.65	10	0.60	0.09
	6.65	14	0.85	0.13
	6.65	12	0.73	0.11
	6.65	10	0.63	0.094
3	6.17	12	0.61	0.10
	6.17	14	0.75	0.12
	6.17	13	0.66	0.11
	6.17	12	0.60	0.10
Average		13	0.65	0.11

The total emissions of NO_x from all gray iron cupolas in the County is 57 pounds or 0.03 ton per calendar day. This figure does not include any emissions from the afterburners on any of the cupolas. NO_x emissions caused solely by combustion taking place in afterburners are discussed further in this report under that heading.

INDUCTION FURNACES

Induction furnaces are used to some extent in the County, usually for the production of special alloys. The size of the heat is usually less than 1000 pounds. With a coil of wire surrounding the crucible in which the metal is to be melted, the metal itself becomes the secondary "coil" of a transformer when electric current is applied to the primary. Heating of the metal takes place rapidly.

The occurrence of some infrequent arcing was thought to be a possible source of NO_x. Samples taken throughout two complete heats, however, show that the NO_x production, if any, is below the limits of detection by

the phenoldisulfonic acid method. Induction furnaces can, therefore, be regarded as insignificant with respect to NO_x production, which is reported as zero in Table I.

HEAT TREAT FURNACES

Heat treat furnaces include a number of common types: box-type, pit, car-bottom, conveyor, pusher, rotary and shaker hearth, muffle, bell-type and elevator, recirculating, controlled-atmosphere furnaces and salt pots. All but the last two of the above-mentioned types of furnaces consist basically of a refractory chamber and a source of heat. The main difference in the atmosphere furnaces is that the atmosphere inside the furnace is controlled to provide a reducing, neutral or oxidizing atmosphere as desired.

The box-type, which may be considered typical of heat treat furnaces except for atmosphere furnaces and salt pots, consists of a chamber which is also the firebox and in which the temperature is maintained within a narrow range. Some of these furnaces are held at relatively low temperatures, of the order of 600°F, while others may be operated at almost any temperature between the low range and the high range, the latter being of the order of 1600°F. The other furnaces of these general types will be operated in essentially the same temperature ranges. The 540 furnaces which make up this group were found to produce NO_x in amounts of 50 pounds or 0.03 ton per day. Table I summarizes the data taken.

The salt pots are similar to crucible-type metal-melting furnaces in that a mixture of nitrite and nitrate salts is placed in a pot which is heated from below until the mixture becomes molten. The molten salt bath is maintained at the desired temperature for the required process. As the temperature approaches the maximum safe limit of approximately 1000°F, some decomposition of the salt occurs. Samples taken at the surface of the molten salt over a range of operating temperatures up to 1000°F indicated NO_x concentrations of 1 to 3 p.p.m. This amount is considered negligible, since the combustion equipment in the furnaces discharged NO_x at concentrations averaging 160 p.p.m. and in amounts averaging 0.10 pound per million Btu of fuel consumed. The 220 salt pots are calculated to produce 140 pounds or 0.07 ton per day of NO_x. Data are summarized in Table I.

The atmosphere furnaces, of which there are 55, frequently are operated with a reducing or neutral atmosphere in the firebox. As might be expected, the NO_x production from these units is low, 7 pounds per day. This amount is considered negligible. Data are shown in Table I.

STEEL MILL "SOAKING PITS"

Steel mill soaking pits are actually furnaces used by steel rolling mills to keep ingots at the proper temperature prior to rolling. Temperatures of approximately 2600°F are maintained with gas-fired burners. The atmosphere within the furnaces is very closely controlled to prevent oxidation of the ingots.

As is shown in Table I, an average emission factor of 0.54 pound per hour per unit was found after testing two such units. The average flue gas concentration of NO_x was found to be 30 p.p.m. Emissions of NO_x from the ten units of this type in Los Angeles County, amount to 0.04 ton per calendar day.

NON-METALLURGICAL FURNACES AND KILNS

This group includes ceramic kilns, boric oxide fusion furnaces and perlite furnaces. The number of installations of these types in Los Angeles County is relatively small, and the total NO_x production from the entire group amounts to less than one-quarter of a ton per calendar day, as is shown in Table I.

CERAMIC KILNS

The ceramic kilns in Los Angeles County may be considered generally as being of two different types: tunnel kilns and beehive kilns. The tunnel kilns are usually used for small, easily-handled items such as pottery, while the beehive type is used mostly for ceramic drainage pipe. In both types, the temperature is carefully controlled at all times to avoid thermal shock.

The tunnel kilns consist merely of long tunnels constructed of some refractory material, with burners introduced through the walls at intervals to provide the desired temperature conditions inside the tunnel. The ceramic material is conveyed through the tunnel at a rate to give the necessary residence time to produce a finished product.

The beehive kilns are large, dome-shaped kilns constructed of refractory brick. They vary in size, with the most common ones being 40 to 60 feet in diameter. Burners are equally spaced around the periphery. A wall is situated inside the kiln with a diameter of approximately four feet less than the outside wall and extending upward to a height of about six feet from the floor. Combustion gases are thereby guided up the inside of the outer wall and to the center of the kiln at the top. The floor is a checkerwork which covers a star-shaped group of ducts beneath the floor. The gases pass downward from the top of the kiln over and through the ceramic material stacked on the floor and through the checkerwork into the ducts. These ducts lead into a main flue which ties into a central stack serving four such kilns. Figure 12 shows the construction of beehive kilns.

There are 64 ceramic kilns on record in Los Angeles County. Approximately 60 per cent of the total number are of the beehive type. Twenty-five per cent of the beehive kilns are large ones, of 1000-ton capacity, with a maximum natural gas consumption of 15,000 CFH. The remaining 75 per cent have a capacity of 40 tons and maximum natural gas consumption of 8000 CFH.

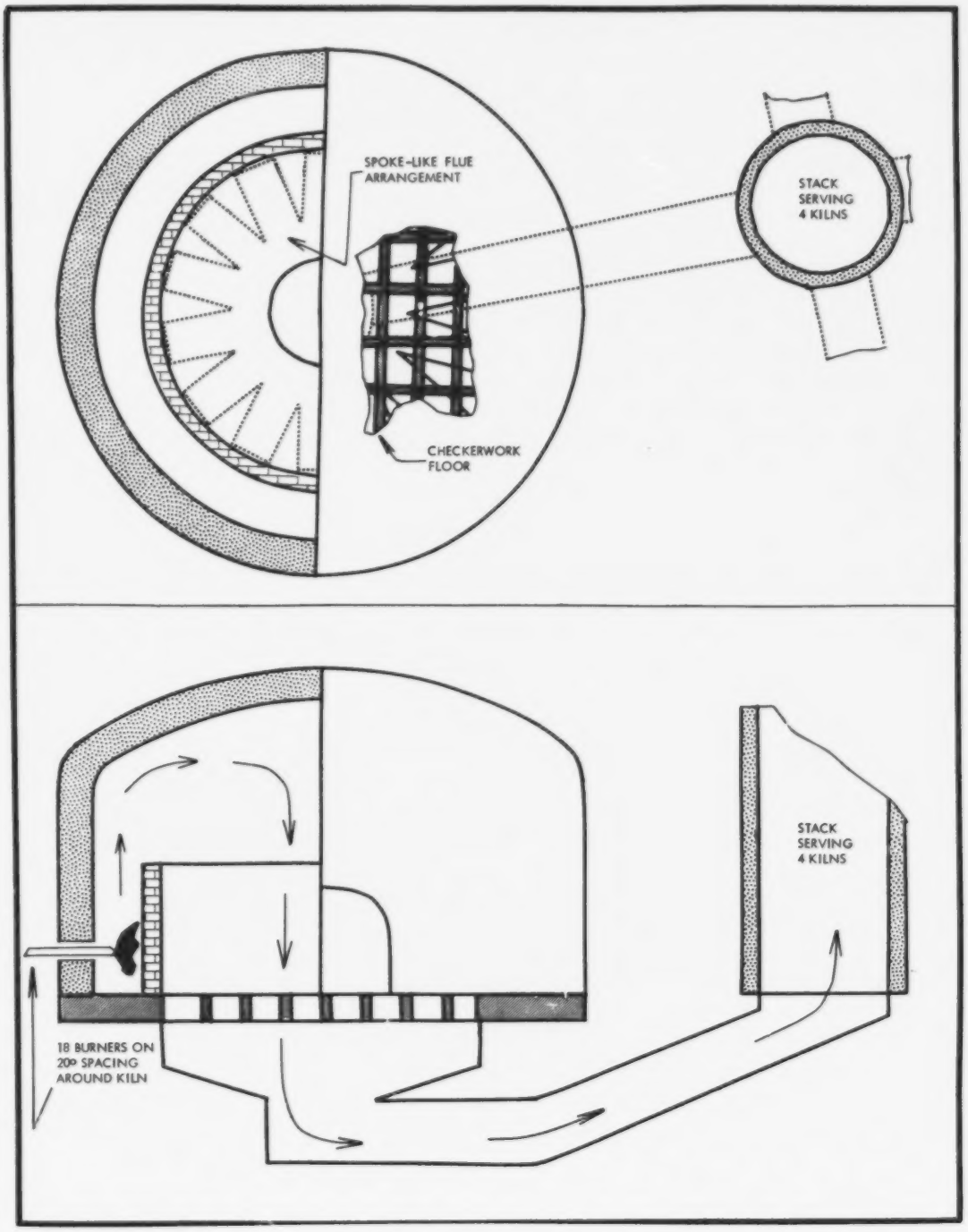
SPOKE-LIKE FLUE ARRANGEMENT
STACK SERVING 4 KILNS
CHECKERWORK FLOOR
STACK SERVING 4 KILNS
18 BURNERS ON 20° SPACING AROUND KILN

Figure 12. This cut-away drawing shows the interior construction of a beehive-type ceramic kiln of the kind used for firing clay sewer pipe.

The production of NO_x from ceramic kilns, as shown in Table I, amounts to 0.23 ton per day from all types. The data are based on the kilns being fired with natural gas. Total emissions average 11 per cent higher on oil furing. However, the proportion of time per year this type of equipment is fired with oil has been considerably less than one per cent.

BORIC OXIDE FUSION FURNACES

Boric oxide fusion furnaces were believed to be potentially significant sources of NO_x production. This type of furnace is a piece of equipment similar to a reverberatory type metal-melting furnace, in which the water of constitution is removed from boric acid and the resulting anhydrous material is fused into a single mass.

There are only two such furnaces in Los Angeles County. One unit was tested to determine NO_x emissions. Both these furnaces are fitted with Venturi scrubbers to control B_2O_3 dust, and there are no places to sample the vent gases between the furnaces and the scrubbers. The sample was taken, therefore, following the scrubber. These furnaces run at high firebox temperatures, and measurable amounts of NO_x would normally be expected. The results suggest, however, either that the NO_x production is small or that the scrubber removes these oxides. Pursuing the scrubbing hypothesis, of course, is a matter for a separate study.

As is shown in Table I, the average concentration of NO_x was 2 p.p.m. which accounts for a total emission of 0.012 pound per hour. Since there are only two units operating twenty-four hours per day, the total emissions are slightly less than one pound per calendar day. This amount is so insignificant that this particular type of equipment may be eliminated completely from consideration as a source of oxides of nitrogen.

PERLITE FURNACES

Perlite products are manufactured by expanding perlite ore which has been crushed and carefully sized. The expansion or "popping" takes place in a high-temperature, gas-fired furnace. Furnace temperatures vary from 1400°F to 2000°F, depending on the character of the perlite rock.

There are ten such perlite furnaces in Los Angeles County, which operate an average of 12 hours per day. The testing of one furnace showed an average of 19 p.p.m. NO_x in exhaust gases with an emission factor of 0.12 pound per hour. The total emission of NO_x from all equipment in this category amounts to 0.007 ton per calendar day.

CHEMICAL PROCESS EQUIPMENT

In Los Angeles County there are but few chemical plants which are potential sources of NO_X. These employ combustion processes or utilize nitric acid and include: phosphoric acid plants, sulfur recovery plants, sulfuric acid plants (contact process), chemical milling tanks for steel, "bright dip" tanks, crystallizers and spray driers. The NO_X production from this entire group amounts to but 0.08 ton per calendar day. Results of analyses are shown in Table I.

PHOSPHORIC ACID PLANTS

There are three phosphoric acid plants in Los Angeles County which produce phosphoric acid by burning elemental phosphorus at an average rate of 4500 pounds per hour.

In the manufacture of phosphoric acid from elemental phosphorus three steps are involved: (1) burning of the phosphorus, (2) hydration of the resulting phosphorus pentoxide, and (3) collection of the mists formed.

Phosphorus is received in tank cars. By means of steam coils in the cars, the phosphorus is melted and pumped to heated storage tanks. A water layer is maintained on top of the phosphorus to prevent contact with the atmosphere. Melted phosphorus is displaced by hot water and pumped into the furnace where it spontaneously burns to phosphorus pentoxide. The hot furnace gases are cooled and hydrated to phosphoric acid in ring-packed towers. The phosphorus furnace operates at a temperature in excess of 1700°F, using 200 per cent excess air. The combustion produces NO_X, about half of which is absorbed in the cooker, hydrator and control scrubber prior to emission to the atmosphere.

Each of the three phosphorus furnaces emits 0.14 pound per hour of NO_X. A total emission of nine pounds of NO_X per day can be attributed to these sources.

SULFUR RECOVERY PLANTS

There are two plants under construction and seven plants now operating to produce elemental sulfur from hydrogen sulfide recovered from oil refinery operations. The operating plants produce 300 tons of sulfur per day.

The process involves burning one-half the H_2S to SO_2 and reacting the SO_2 with the other half of the H_2S to produce water and elemental sulfur. From 93 to 96 per cent recovery is obtained.

It was found that 0.05 pound of NO_x is emitted per ton of sulfur produced. Total emissions are 15 pounds per calendar day.

SULFURIC ACID PLANTS (CONTACT PROCESS)

In the contact process, sulfur, H_2S or acid sludge may be the starting raw materials. These are burned to produce a gas stream containing SO_2. The SO_2 is converted to SO_3 and absorbed in concentrated sulfuric acid. Test data revealed that an average of 0.01 pound of NO_x is emitted per ton of sulfuric acid produced. Estimated acid production is 1000 tons per day. On this basis, the total NO_x emission amounts to 10 pounds per calendar day.

STEEL CHEMICAL MILLING TANKS

Chemical milling is a recently developed process for removing a desired portion of metal from an object chemically instead of mechanically to produce a predetermined shape.

The operation is carried on under carefully controlled conditions of temperature and acid concentration. A solution consisting of approximately 650 pounds of 10-N nitric acid in 1000 gallons of water along with a quantity of 8-N sulfuric and 10-N hydrochloric acid is placed in a rubber or plastic-lined tank. The solution is maintained at 138°F. Steel parts which have been masked to expose only the desired surface, are immersed in the tank for a time calculated to be necessary to remove the required amount of metal.

Some of the variables expected to influence the amount of NO_x formed are:

1. Temperature of the solution,
2. Concentration and quantity of nitric acid present,
3. Area of steel surface immersed in the solution,
4. Area of solution surface exposed to the atmosphere.

Since the solutions used and the temperature at which they are maintained are virtually the same in all steel chemical milling operations,

these factors may be discounted as influencing the NO_x production to any significant degree.

It should be realized that the area of steel surface immersed, however, can vary appreciably. Although not entirely accurate, the method of evaluating NO_x emissions from this source is based upon the assumption that a normal load will have a proportionately larger area of steel exposed in a large tank with a greater quantity of HNO_3 than normal load in the smaller tank that was tested. It was found the NO_x emissions averaged 0.062 pound per hour per 100 pounds of nitric acid in the tank.

There are four tanks with a total capacity of 19,348 gallons containing a total of 12,578 pounds of HNO_3. The usage factor is 8.5 hours per calendar day. Total NO_x emissions from all steel chemical milling tanks are calculated to be 65 pounds or 0.03 ton per calendar day.

BRIGHT DIP TANKS (NITRIC ACID)

The final metal surface treatment for copper and its alloys is generally bright-dipping. This treatment leaves the surface smooth and brilliant, and it is universally used prior to electro-plating.

The compositions of bright-dip solutions vary. However, they usually consist of mixtures of sulfuric and nitric acids to which small amounts of water and hydrochloric acid have been added.

Similar operations (i.e., dipping of metals into nitric acid solutions) are referred to as acid pickling, copper stripping, passivating of stainless steel, acid surface treatment and chemical cleaning. Even aluminum is acid-pickled in nitric acid to remove smudge following alkali dips. Nickel-silver alloys are bright-dipped, as well as zinc, cadmium, monel and some brasses.

As metals are immersed in or withdrawn from such nitric acid-containing vessels, observable clouds of brown nitrogen dioxde gas are evolved. There are many small tanks utilized in Los Angeles County which contain weak solutions (10 per cent) of nitric acid. These may be referred to as "bright-dip tanks" but are excluded from this project inventory since the usage factor is low, the quantity of NO_x is small and the total number of units is less than 75. For example, one such tank for chemical cleaning of aluminum prior to brazing was investigated. The emissions amounted to 0.03 pound of NO_x per hour, which is negligible.

It is estimated that there are 12 strong acid tanks in Los Angeles County utilized for copper stripping, passivating stainless steel and acid pickling. Investigation shows that an average of 0.7 pound per hour of NO_x is emitted from these tanks, most of which are equipped with water scrubbers. The tanks are used six hours per calendar day. The total emission of NO_x from these tanks amounts to 50 pounds per calendar day.

CRYSTALLIZERS

In the production of sodium hexametaphosphate, a solution of soda ash and phosphoric acid is fed into a direct-fired, gas-burning furnace. In the furnace the solution forms a high temperature melt which is subsequently solidified, broken and packaged.

Investigation of the combustion products from the 2200°F flame revealed a loss of 0.17 pound per hour of NO_x. Since there is only one hexametaphosphate crystallizer in Los Angeles County, the total daily loss of NO_x to the atmosphere from this type of equipment, based on 8 hours' operation per calendar day, is 1.4 pounds, which may be considered insignificant.

SPRAY DRIERS

Spray driers are widely used in the chemical, pharmaceutical and food industries. They operate on the principle of creating a highly dispersed liquid state in a high-temperature gas zone. Because of the high surface-volume ratio of the dispersed liquid droplets, drying time is considerably less than one second for high temperature operation.

Every spray drier is composed of the following essential elements: (1) an air heater, (2) a pumping system, (3) an atomizer, (4) a drying chamber, (5) a product-removal system, and (6) a dust-collection system. Spray driers are of particular interest to this project because of the heater. The quantity of fuel required to heat the rather enormous volumes of air which must pass through the drying chamber was believed to indicate that the amount of NO_x formed might be appreciable.

Two large detergent spray driers were investigated. Table IX lists operational data and results of investigations.

TABLE IX

NO_x EMISSIONS FROM SPRAY DRIERS

Spray Drier	Heat Input Btu/Hr	Exhaust Gas Vol. SCFM	Per Cent CO_2 (Stack Cond.)	P.P.M. NO_x (Stack Cond.)	NO_x Emissions Lbs/Hr	NO_x Emissions Lbs/10^6 Btu
A	12,990,000	20,800	1.10	6.7	1.02	.08
B	16,800,000	34,000	0.87	6.4	1.58	.09

There are five large detergent spray driers in the County, plus a number of small spray driers being utilized in other chemical, pharmaceutical and food industries. The total number of all spray driers is estimated to be the equivalent in NO_x production of between six and seven large driers. The census figure is reported as six. The average heat requirement for detergent spray driers is 15,000,000 Btu per hour.

The emission of NO_x from detergent spray driers is 30 pounds per day or 0.085 pound per million Btu; the emission of NO_x from other spray driers is estimated to be nine pounds per day, making the estimated total emission of NO_x from all such driers in Los Angeles County 40 pounds per day.

GENERAL INDUSTRIAL EQUIPMENT

This group includes boilers under 500 h.p. in size, small oil heaters in refineries, industrial ovens, degreasers, welding equipment and small incinerators (up to 1000 pounds per hour burning capacity). Results of tests of these units are summarized in Table I. The total NO_x production from this equipment is 20 tons per day in winter and 15 tons in summer, making this group the second most significant of all the small sources.

SMALL BOILERS

The boilers to be considered in this category are boilers rated up to 500 horsepower. The distribution curve of the number of boilers in each horsepower range in Figure 13 shows that 98 per cent of the boilers, exclusive of steam generation plants, fall into this category.

The graph in Figure 14 shows the rate of heat input required to attain a given horsepower rating. From this, the amount of liquid or gaseous fuel may be calculated.

An average of a number of tests covering all types of boilers and the complete range of horsepower ratings produced an emission factor of 0.14 pound per million Btu for natural gas and 0.49 pound per million Btu for fuel oil.

All boilers up to and including 500 horsepower normally produce NO_x emissions less than the five pounds per hour chosen as the limit for small sources. Five-hundred-horsepower boilers fired with oil will exceed this limit slightly, but in single instances there may also be a 600-horsepower boiler that will be under five pounds per hour; and some 400-horsepower boilers may exceed the five pounds per hour. The 500-horsepower rating, however, appeared to be the most likely point to divide the category based on average emissions.

The census of boilers is based upon three different methods of operation according to the type of fuel burned. The first group includes those on a firm gas supply. These boilers do not require standby oil-burning equipment. The boilers in the second group are on an interruptible gas supply and must have standby oil-burning equipment in the event the gas supply is curtailed. Table X shows the curtailment blocks for one interruptible schedule and the number of calendar days on which curtailment

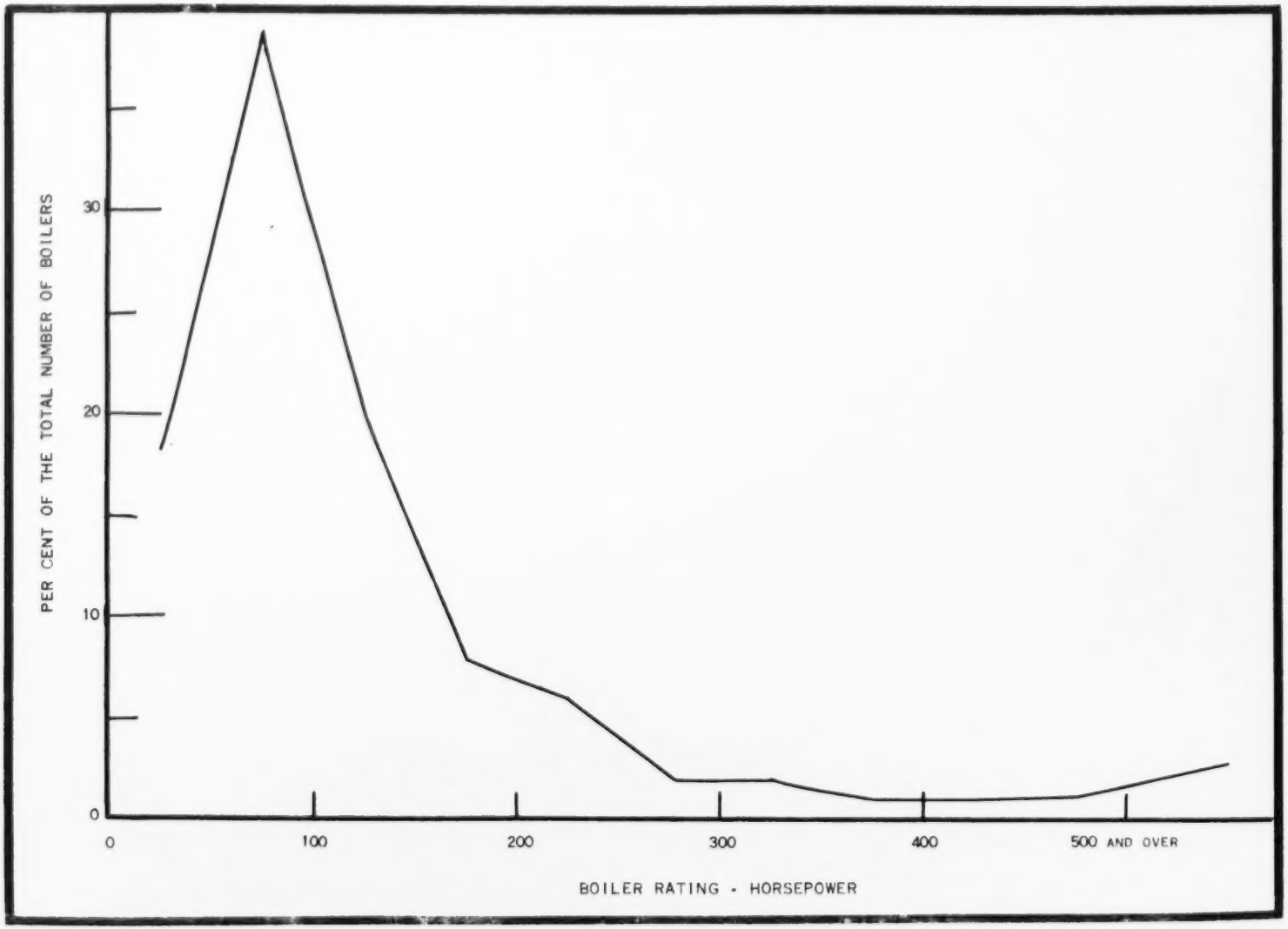

Figure 13. This graph shows the per cent of the total number of boilers in each size range. Ninety-eight per cent of all the boilers in Los Angeles County are rated at less than 500 horsepower.

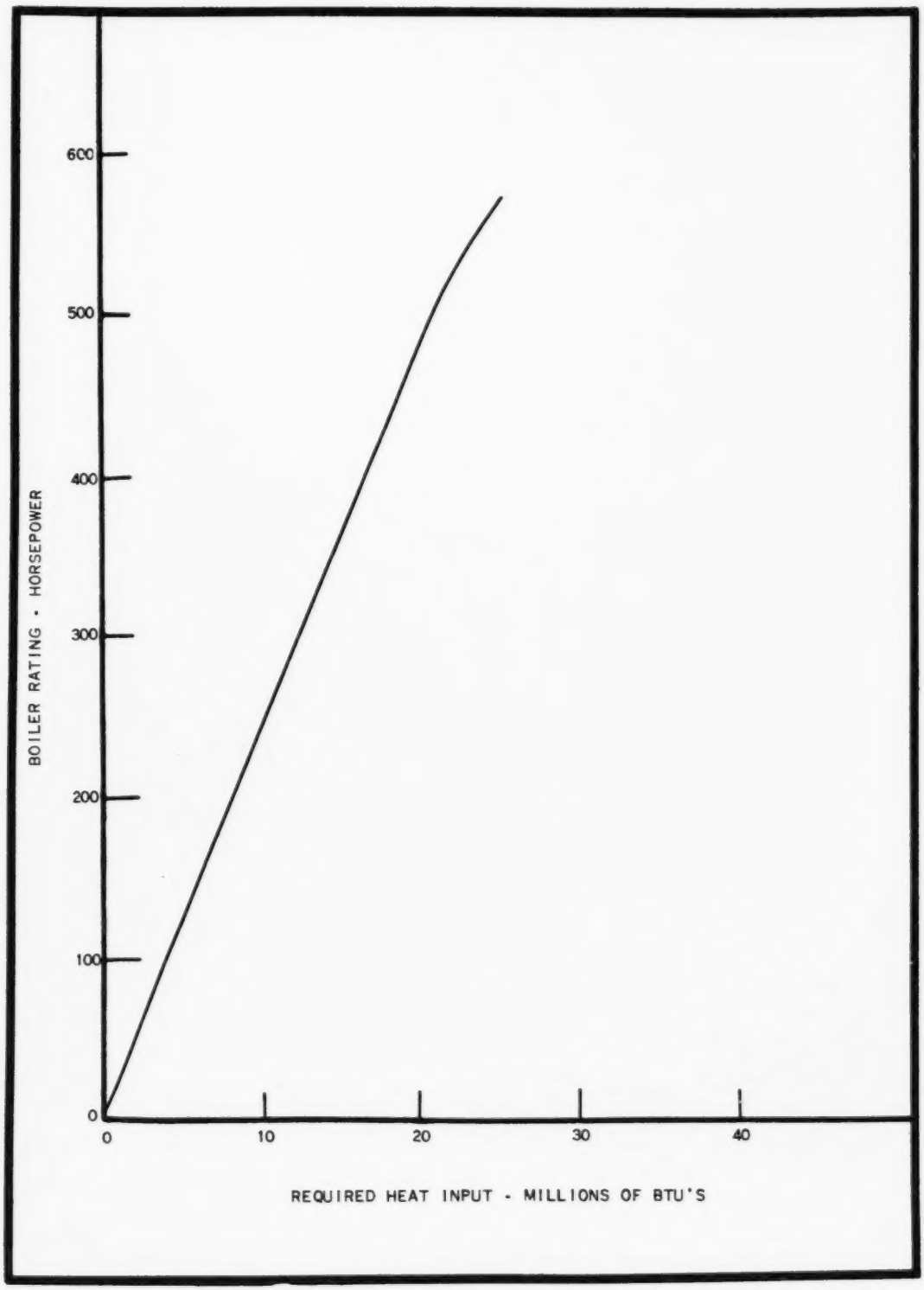

Figure 14. This graph shows boiler rating as a function of required heat input.

TABLE X

CURTAILMENT SCHEDULE G-50 FOR INTERRUPTIBLE GAS CONSUMERS IN LOS ANGELES COUNTY

	Curtailment Blocks MCF*/Month Consumption				
	A	B	C	D	E
	N.A.**	above 44571	13251-44571	2751-13250	0-2750
No. of 24-hour days curtailment during 1959		8.86	8.73	2.19	0

* Thousand cubic feet

** Not applicable to this study

occurred during the past year. Boilers with a rating of up to 250 h.p. will fall into Block E of schedule G-50 and the remaining boilers up to 500 h.p. rating will fall into Block D. It may be seen that gas curtailment forced fuel oil to be burned in the boilers of these classifications less than one per cent of the time during 1959. For this reason, the boilers in the interruptible rate classification were considered to be burning gas 100 per cent of the time for the purpose of calculating NO_X emissions. The third group includes boilers which burn fuel oil exclusively and which have no provisions for burning natural gas. Tables XI, XII and XIII summarize the maximum hourly rate of NO_X emissions from boilers in each of the three groups. Calculations for these tables are based on concurrent usage of all boilers.

Boilers in the three classifications differ in their usage. Calculations of total NO_X emissions for each group of boilers as shown in Table I are based on annual and seasonal fuel consumption data. Total NO_X emissions from all classifications of boilers amount to 18 tons per day during the winter and 14 tons per day during the summer. The annual average is 16 tons per day.

TABLE XI

NO_x EMISSIONS FROM BOILERS IN LOS ANGELES COUNTY
ON FIRM GAS SERVICE WITH NO OIL STANDBY

H.P. Range	Per Cent of Total	No. of Boilers	Gas Consumed SCFH/Unit	NO_x Lbs/Million Btu	NO_x Lbs/Hr/Unit	Total NO_x** Lbs/Hr
0- 50	18	540	1000	0.14	0.15	83
51-100	39	1170	2730	0.14	0.42	420
101-150	20	600	4820	0.14	0.74	440
151-200	8	240	6450	0.14	0.99	240
201-250	6	180	8360	0.14	1.3	230
251-300	2	60	10500	0.14	1.6	96
301-350	2	60	12300	0.14	1.9	110
351-400	1	30	14150	0.14	2.2	67
401-450	1	30	15900	0.14	2.2	66
451-500	1	30	20000	0.14	3.1	94
501 & over	2	60				
Totals	100	3000*				

* Exclusive of power plant boilers.
** Calculation based on concurrent usage of all boilers. Numbers rounded off to two significant figures.
*** Emission data shown for small sources only.

TABLE XII

NO_x EMISSIONS FROM BOILERS IN LOS ANGELES COUNTY
ON INTERRUPTIBLE GAS SERVICE (OIL STANDBY REQUIRED)
BUT BURNING ONLY GAS

H.P. Range	Per Cent of Total	No. of Boilers	Gas Consumed SCFH/Unit	NO_x Lbs/Million Btu	NO_x Lbs/Hr/Unit	Total NO_x** Lbs/Hr
0- 50	18	410	1000	0.14	0.15	61
51-100	39	890	2730	0.14	0.42	370
101-150	20	456	4820	0.14	0.74	340
151-200	8	182	6450	0.14	0.99	180
201-250	6	137	8360	0.14	1.3	180
251-300	2	45	10500	0.14	1.6	73
301-350	2	45	12300	0.14	1.9	85
351-400	1	23	14150	0.14	2.2	50
401-450	1	23	15900	0.14	2.2	50
451-500	1	23	20000	0.14	3.1	71
501 & over	2	46				***
Totals	100	2280*				

* Exclusive of power plant boilers.
** Calculation based on concurrent usage of all boilers. Numbers rounded off to two significant figures.
*** Emission data shown for small sources only.

TABLE XIII

NO_X EMISSIONS FROM BOILERS IN LOS ANGELES COUNTY
BURNING FUEL OIL ONLY

H.P. Range	Per Cent of Total	No. of Boilers	Oil Consumed GPH/Unit	NO_X Lbs/Million Btu	NO_X Lbs/Hr/Unit	Total NO_X** Lbs/Hr
0- 50	18	95	7.75	0.49	0.54	51
51-100	39	207	21.13	0.49	1.5	310
101-150	20	106	37.32	0.49	2.6	280
151-200	8	42	50.00	0.49	3.5	150
201-250	6	32	64.79	0.49	4.5	140
251-300	2	11	80.99	0.49	5.6	62
301-350	2	11	95.07	0.49	6.6	73
351-400	1	5	109.86	0.49	7.7	38
401-450	1	5	123.24	0.49	8.6	43
451-500	1	5	154.93	0.49	11	55
501 & over	2	11				
Totals	100	530*				

* Exclusive of power plant boilers.
** Calculation based on concurrent usage of all boilers. Numbers rounded off to two significant figures.
*** Emission data shown for small sources only.

SMALL REFINERY HEATERS

The type of equipment considered in this category is any heater in a refinery consuming less than two million cubic feet per day of natural gas or its equivalent.

A heater may be described generally as being a brick firebox inside of which are metal tubes through which a liquid is passed to pick up a desired amount of heat. Heaters may be fired with refinery-make gas, natural gas, fuel oil or a combination thereof.

There are a total of 283 small heaters in Los Angeles County, comprising 81 per cent of the total number of heaters. The average usage factor for these heaters is 22 hours per calendar day. Each heater produces an average of 3.2 pounds per hour of NO_x. All the small heaters together produce 2000 pounds or one ton of NO_x per calendar day. The average concentration of NO_x from these heaters is 47 p.p.m. at stack conditions. The emission factor per million Btu of fuel is 0.06 pound.

BAKING AND DRYING OVENS

Gas-fired industrial baking and drying ovens are of two general types: direct-fired and indirect-fired. Both types are usually box-like in shape with insulated walls. Individual units will vary greatly in details of construction and operating conditions. The direct-fired ovens have burners located in the oven proper where products of combustion are in contact with the materials being heated. The indirect-fired ovens are equipped with a separate combustion chamber, which is used to heat air. The hot air is circulated through the oven proper with a fan. Products of combustion are vented directly to the atmosphere and do not contact the materials in the oven.

Some of the more common operations for which ovens are used are bakery ovens (for producing bread, cakes, pies, etc.), core ovens used to cure resin or linseed binders in sand cores for the foundry industry, paint baking ovens, plastic curing ovens, rock wool drying ovens and water dry-off ovens. A representative number of the above type of ovens were tested over a range of operating temperatures and sizes. The sizes ranged from a fuel consumption of 60 CFH in the smaller ovens to 8,000 CFH in the larger ones. Operating temperatures covered a range of 180°F to 650°F. The average size oven will require an input of 1,200,000 Btu per hour.

Three-fourths of the ovens operate from 25 to 40 hours per week. Fifteen per cent are in use more than 40 hours per week and ten per cent are used less than 25 hours per week. An average usage factor is four hours per calendar day. Projecting the 1958 figures supplied by the gas-distributing utility companies' oven census and the total gas consumed by these ovens to the 1960 basis, we find that there are 2800 ovens consuming a total of 12,200,000 cubic feet of gas per day.

Since the tests revealed that the operating temperature did not appear to be an influencing factor other than its effect on the total gas consumption, the most convenient parameter for evaluation NO_X emissions was on the basis of pounds of NO_X per million Btu of gross heating value. The data fall into the range of 0.03 to 0.11 pound per million Btu and average 0.082 pound per million Btu gross heating value. Concentrations of NO_X in the exit gases were found to range from slightly below 10 p.p.m. to 40 p.p.m.

The total NO_X emissions for all ovens is 1100 pounds or 0.55 ton per calendar day. This does not include any emissions from afterburners serving ovens. Those quantities are included in the section on afterburners.

DEGREASERS

A very popular method of grease removal is known as vapor degreasing. This method consists essentially of two phases: a liquid phase and a vapor phase. The solvent is usually stabilized trichloroethylene. The solvent is heated to boiling (trichloroethylene, 188°F) in a suitable container, the upper portion of which is cooled by means of coils through which water is circulated.

The article to be degreased is immersed in the hot liquid phase where the largest portion of greasy contaminants is removed. It is then brought into the hot vapor phase where clean solvent condenses on the relatively cooler part and thus removes any grease still remaining.

For purposes of this study, interest lies in the emission of NO_X from the direct combustion of fuel to heat the degreasing solvent.

There are an estimated 1400 degreasers in Los Angeles County. One thousand of these are direct gas-fired. Thirty per cent of the degreasers are either steam or electrically heated. Degreasers are utilized on an average of 5.3 hours per calendar day.

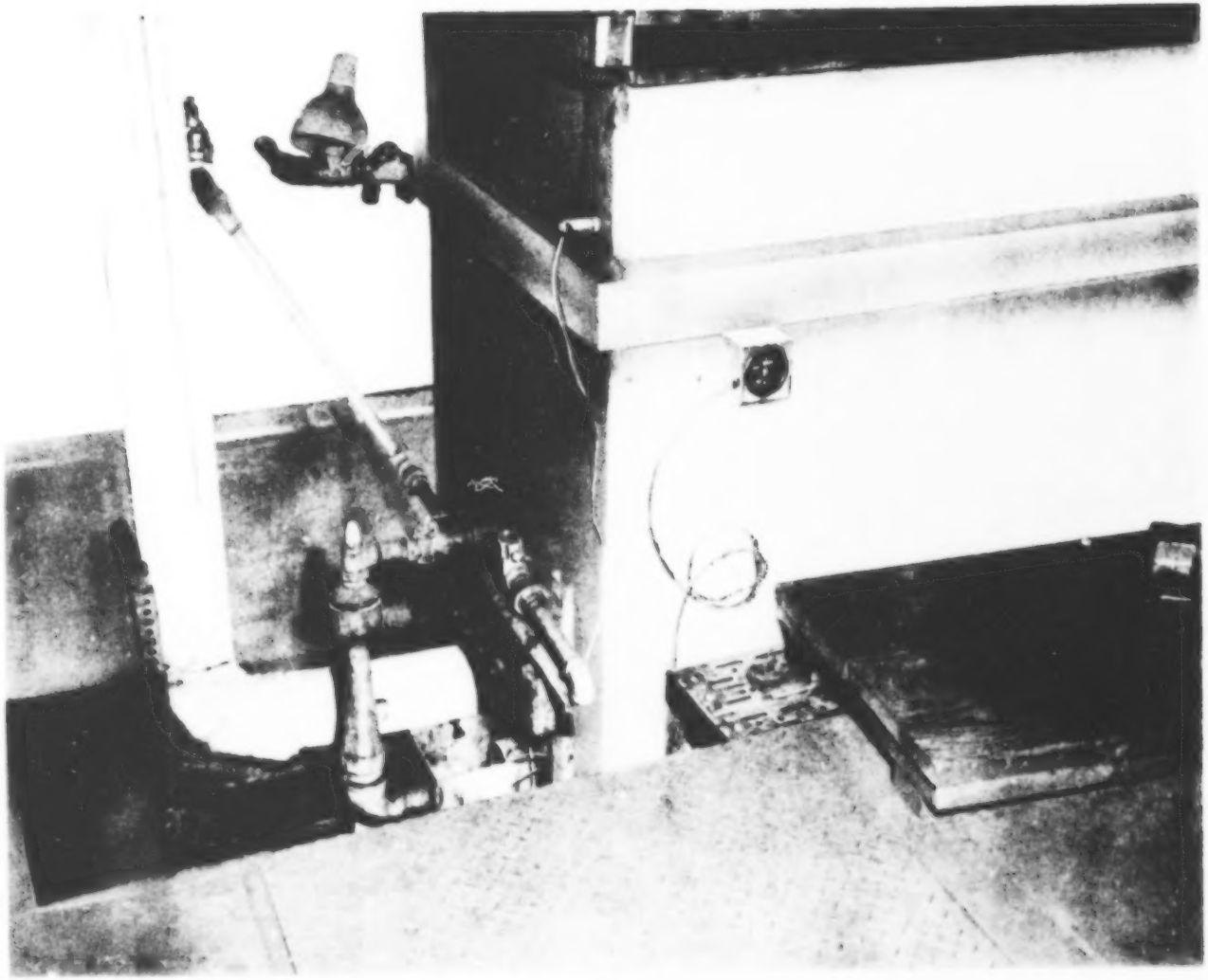

Figure 15. This vapor degreaser is heated by a gas burner which fires into a space below the solvent tank. Combustion gases are vented through the flue on the left side of the picture.

Tests of degreaser heaters of several sizes, and under extreme firing conditions, indicate that 0.004 pound of NO_x is emitted per hour to the atmosphere from the average gas-fired degreaser. This may also be evaluated on the basis of 0.018 pound per million Btu gross heating value. Thus, 21 pounds or 0.01 ton per calendar day of NO_x is emitted from this source in Los Angeles County.

WELDING EQUIPMENT

The type of industry in Los Angeles County has dictated the ratio of welding methodology utilized, i.e., oxy-acetylene, arc-air and inert arc welding. Inert arc-welding using helium, argon or CO_2 constitutes about 30 per cent of the total. Oxy-acetylene and arc-air welding represent the other 40 per cent and 30 per cent, respectively. An estimated 150,000 machines of all types are in use in Los Angeles County for an estimated six minutes per day (average). On this basis, all machines constitute 15,000 operating hours per day. A total of 825,000 pounds of welding rod are utilized per month.

In arc welding, NO_x is formed thermally at the arc. The production of these oxides, therefore, might be represented in samples taken in the fume stream 5 to 6 inches from the arc. Mean nitrogen dioxide concentrations observed by Fay, et al.[6] during various methods of welding, utilizing different base metals, gas and current are summarized in Table XIV.

Assuming that 10 cfm of exhaust gases containing 10 p.p.m. NO_x are emitted to the atmosphere per machine, the emissions of these oxides by all machines in Los Angeles County are calculated to be 11 pounds or 0.005 ton per calendar day.

TABLE XIV

NO_x CONCENTRATIONS FOR VARIOUS WELDING OPERATIONS

Welding Method	Base Metal	Gas	Current Amperes	Mean NO_x Concentrations, P.P.M.*
Inert arc	Stainless steel Aluminum Bronze	Argon CO_2	180 AC 150-260 DC	21.5 1.5
Arc-air	Stainless steel Mild steel	Air	120-300 DC	1.5
Oxy-acetylene	Mild steel	O_2-Acet.		9.0

* Based on 120 samples.

Note: Volumes used to exhaust the welding fumes were of the order of 10 cfm.

SMALL INCINERATORS

In any urban area the disposal of combustible waste material becomes a problem. The accepted solution for many years was merely to place the waste in a receptacle, such as a barrel, with a few holes in it to provide draft, and to touch a match to it. Later, a more permanent device, usually made of bricks or concrete, with a charging door, a grate, draft openings and a short stack came into being and was known as the "backyard incinerator." In Los Angeles County, however, it became illegal to dispose of combustible refuse in this manner on October 1, 1957. Since that time only approved multiple chamber incinerators may be used to burn combustible rubbish.

Multiple chamber incinerators are usually considered as being one of two types: retort and "in-line" multiple chamber incinerators. A cut-away diagram[7] of each type may be seen in Figures 16 and 17.

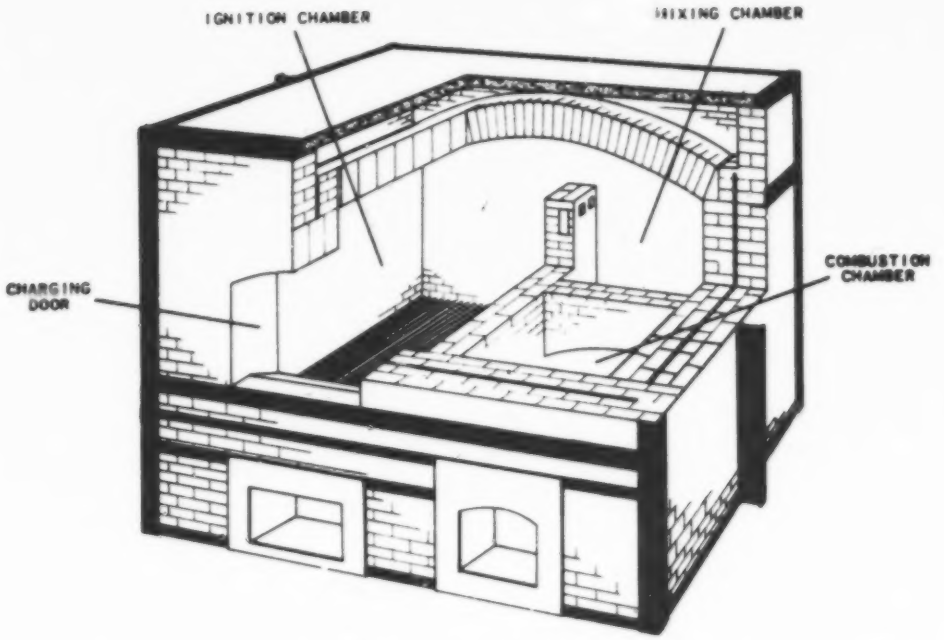

Figure 16. In this retort-type multiple chamber incinerator the combustion gases pass over the flame port at the rear, down through the mixing chamber and up through the combustion chamber to the stack.

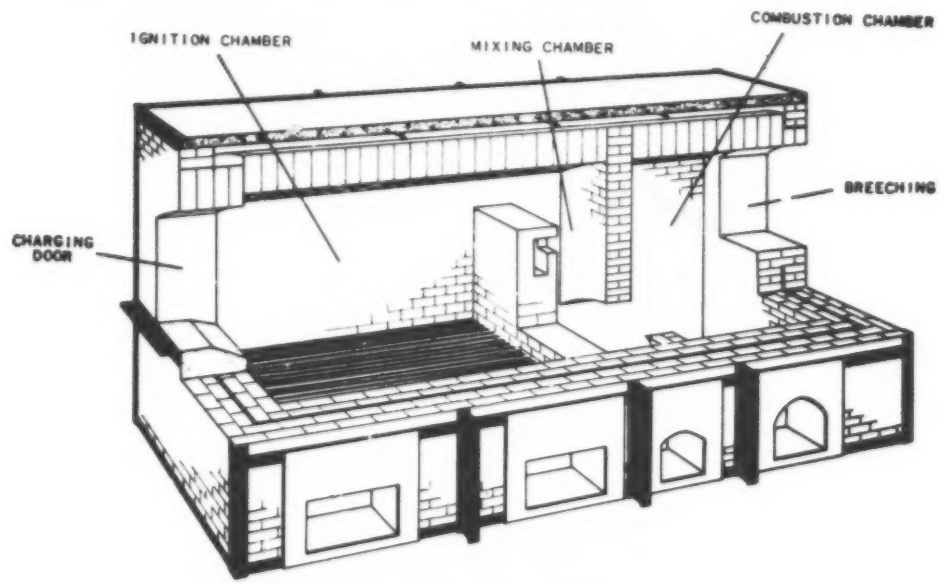

Figure 17. This cut-away drawing shows an in-line type multiple chamber incinerator. This design is best for burning more than 750 lbs/hr of rubbish.

Ninety-six per cent of the total number of incinerators in Los Angeles County are rated at less than 1,000 pounds per hour capacity. Each of these produces less than five pounds per hour. Details of NO_x emissions are given in Table I.

There are several factors which may affect the emissions of NO_x from multiple chamber incinerators to some degre. Rose, et al.[8] state that excess combustion air was the variable having the greatest effect on the discharge of NO_x. No quantitative values were assigned, however. Since 90 per cent of the incinerators in Los Angeles County are fired using 300 per cent excess air, this variable becomes insignificant. Another factor to be considered is the temperature in the combustion chambers. Most of the incinerators will have gas temperatures close to the average of 1000°F when 300 per cent excess combustion air is used.[7] This also then assumes an unimportant role in the overall consideration.

The type of material charged to the incinerator will have some effect as well as the period of operation. Emissions appear to be greatest during light-off and least during burndown. However, since these two conditions only represent a small portion of the total operation, the data were evaluated from tests conducted under normal operating conditions.

AFTERBURNERS

Certain types of air pollution control problems are best solved by incineration of the off-gases. The afterburners used are designed somewhat differently from ordinary incinerators for waste materials, since the material to be burned is in the gaseous state. Figures 18 and 19 show two types of afterburners. A number of other designs can be employed, but, in general, the afterburners are designed in such a manner as to mix the contaminants thoroughly with the flames, providing a minimum residence time of about 0.25 second and a mixing velocity of the order of 10 to 20 feet per second. A refractory lining protects the steel shell from the operating temperatures in the range from 1100°F to 1500°F. The contaminated gas stream may be introduced into the afterburner below a multi-jet burner and mixed with the flame as it passes up through it or the contaminated gas stream may be introduced just above two or more atmospheric or premix burners firing tangentially into the combustion chamber. The swirling action provides adequate mixing of the gas stream with the flow.

Most of the afterburners are used to incinerate contaminated gas streams from:

1. Flue-fed incinerators,
2. Meat packing and rendering plants,
3. Industrial plants emitting organic solvents,
4. Metal melting, smelting and reclaiming operations.

At the present time there are 550 afterburners in operation in Los Angeles County. Of this number, 250 are found to be serving flue-fed incinerators. NO_x emissions that can be attributed to the afterburners alone, exclusive of the incinerators, amount to 0.10 pound per hour. When evaluated on the basis of gross heating value, the amounts range from 0.04 to 0.11 pound per million Btu giving an average value of 0.08 pound per million Btu gross heating value. The usage factor on these afterburners averages 1/2 hour per calendar day. The total NO_x emissions are 12 pounds per calendar day.

The remaining 300 afterburners are used 12 hours per calendar day. They produce 0.15 pound of NO_x per hour or 0.05 pound of NO_x per

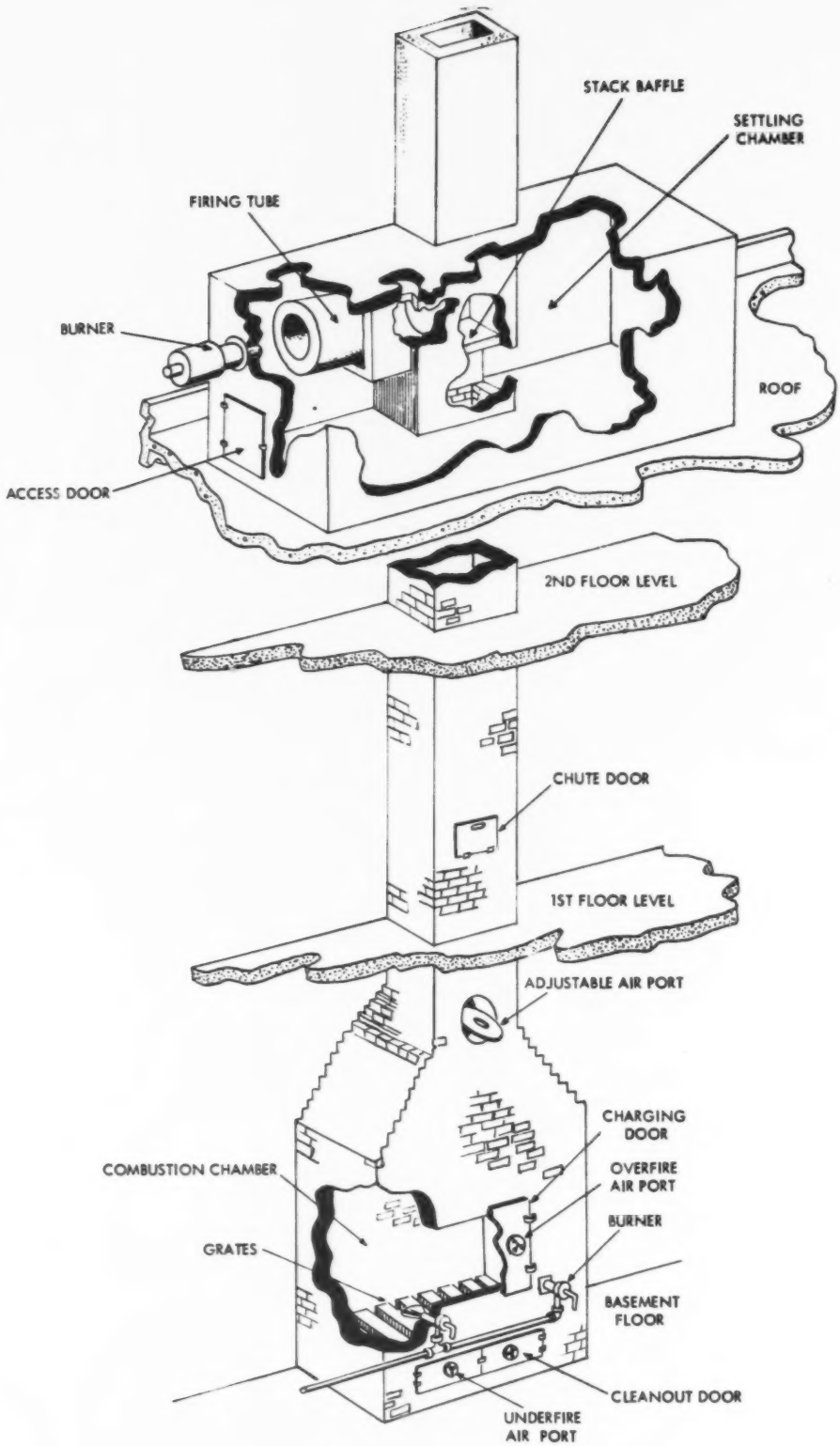

Figure 18. Smoke and fly ash from a chute-fed incinerator in an apartment building can be controlled by an afterburner located on the roof.

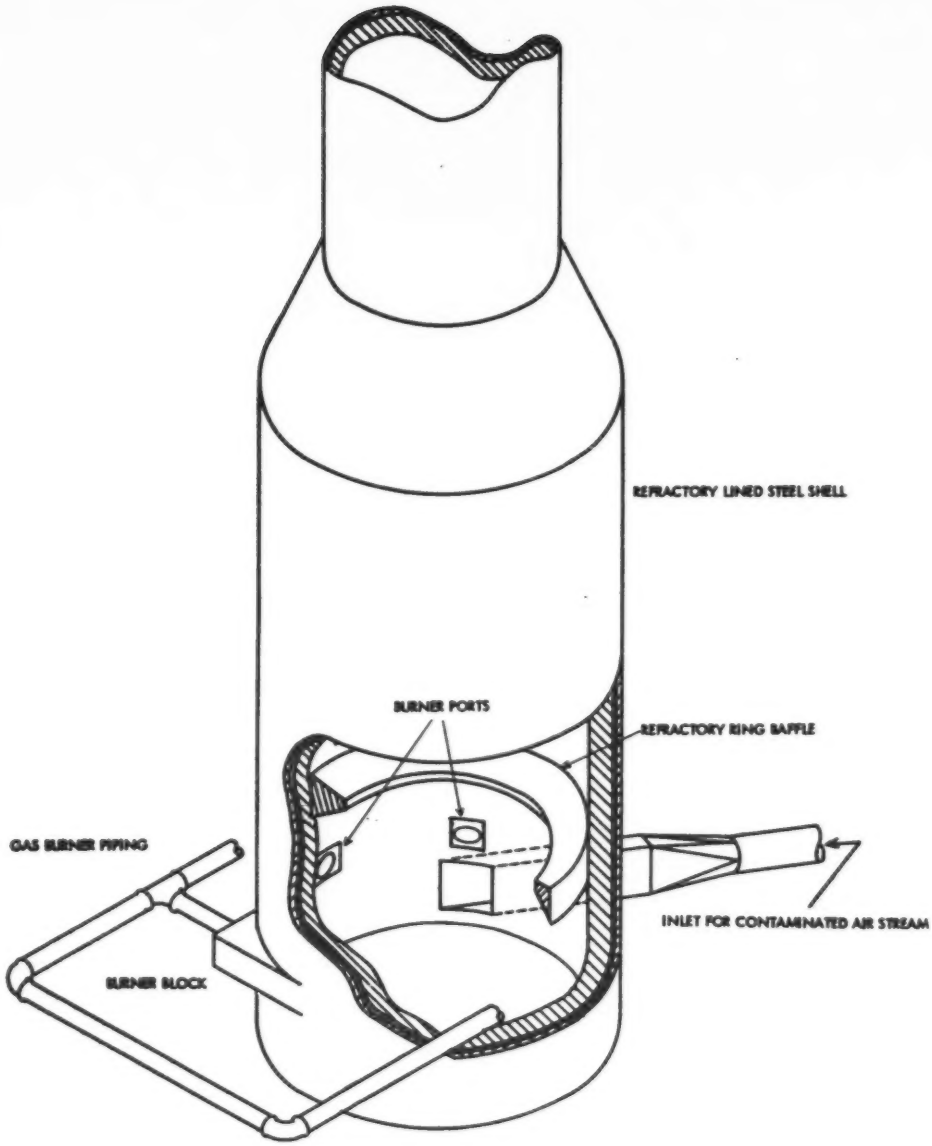

Figure 19. Varnish cooker emissions are exhausted to an afterburner consisting of a firebox with four tangentially-mounted gas burners.

million Btu gross heating value. The total NO_x emission from these afterburners is 540 pounds per calendar day.

The total emission from all afterburners, exclusive of the equipment they serve, is 550 pounds or 0.28 ton per calendar day.

ELECTRIC PRECIPITATORS

Electric precipitators were tested to determine if the arcing or corona discharge was great enough to produce significant amounts of NO_x. It had been estimated that the contributions, if any, were small. On this basis, several installations were tested, such as the precipitators serving a gray iron cupola, a galvanizing operation and a large carbon monoxide boiler. These installations were tested under normal operating conditions. With the amount of arcing occurring during such operating conditions, no increase in NO_x between the inlet and outlet of the precipitator was found in any of the installations.

It could be possible that some NO_x might be formed, if extremely heavy arcing occurred during periods when the precipitator was not functioning properly. However, these periods will be at such infrequent intervals and of such short duration that any NO_x formed may be considered a negligible contribution to the overall problem.

It may be concluded that electric precipitators do not contribute enough NO_x to be considered a significant source.

MISCELLANEOUS EQUIPMENT

There are a number of miscellaneous types of equipment capable of producing NO_X. Although the numbers of units are relatively small, several tests were made to determine the orders of magnitude involved in the production of NO_X. The types of equipment to be considered in this section are those that do not bear any particular relationship to any of the more general classes of equipment discussed above or are thought to be of such small importance that a special section devoted to their evaluation would not be warranted. The purposes for which the equipment described in this group are used are fairly specific in their application. Test results are summarized in Table I.

REFINERY FLARES

Although refinery flares are essentially a type of afterburner, they are such a specialized case that it was felt they should be discussed separately.

The purpose of a flare in present day refineries is to prevent an accumulation of explosive vapor in hazardous locations by incinerating it in a controlled location. Most of the gases come from emergency releases caused by excessive pressures in operating units. Some gas still goes to the flare from intermittent blowdown operations but the tendency is to put most of the gas from normal operation into the "refinery-make" gas system and burn it as fuel.

The unpredictable behavior and frequently inaccessible locations of flares make their testing somewhat hazardous, as can be predicted by viewing Figure 20. The one accessible flare, which was tested, showed approximately 5 p.p.m. NO_X produced by the pilot burner and 25 p.p.m. produced by the flare in operation.

There are approximately 40 flare installations in Los Angeles County, all of which have continuous pilot flames. These pilots consume an estimated 675,000 standard cubic feet of gas per day, giving a total emission of NO_X from pilots of 10 pounds per day. The total gas burned as waste and during emergencies is approximately 1,380,000 standard cubic feet per day, producing 100 pounds of NO_X. The total average emission from flares is 110 pounds of NO_X per day.

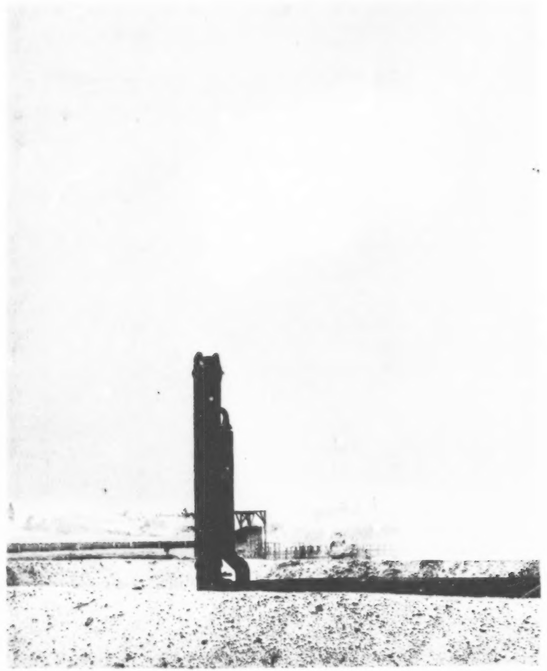

Figure 20. Steam injection is used in this type of refinery flare to produce turbulence resulting in the hot, smokeless flame visible here.

SMOKE GENERATORS FOR MEAT CURING

An old time standard method of curing meat is that of subjecting the meat to an atmosphere of hardwood smoke for a period of time under controlled conditions of temperature and humidity.

Modern day equipment consists of a smoke generator to produce smoke that will be used in a bank of one to four meat smokehouses. The generators function either by spreading damp hardwood sawdust on a plate or conveying it through a tube that is heated by either a gas flame or electricity. In the other type, the sawdust itself is ignited and allowed to smolder.

There are 61 such generators in Los Angeles County. Over 50 per cent of this number are of the type in which the sawdust itself is ignited and allowed to smolder. Of the remainder, some are electrically heated and some are gas-fired. The gas consumption is quite low for these units.

It was found that the NO_x concentration in the smoke produced was between 1 and 2 p.p.m. On a pounds-per-hour basis, the emissions are insignificant. From the gas-fired generators, the concentration and pounds per million Btu are the same as any gas appliance. The total weight discharged per hour from the average generator is 0.05 pound. The average use is 16 hours per calendar day. Total emissions from the 26 gas-fired generators amount to 23 pounds or 0.01 ton per calendar day.

GALVANIZING KETTLES

Galvanizing kettles are generally large steel tanks in which metallic zinc is melted and held for a hot dipping operation. They are supported on a refractory foundation. Burners inserted through the walls at a level below the tank provide the necessary heat. An average size for these kettles is about 4 feet wide x 20 feet long x 5 feet deep, as is shown in Figure 21. The molten zinc is maintained at a temperature from 840°F to 860°F. A thin layer of molten lead is frequently maintained in the bottom of the kettles to segregate dross. Clean, oxide-free iron or steel parts, sheets, or fencing are dipped into the molten zinc to provide a corrosion-resistant protective coating. A flux of zinc ammonium chloride is used to assist in providing a good bond between the two metals.

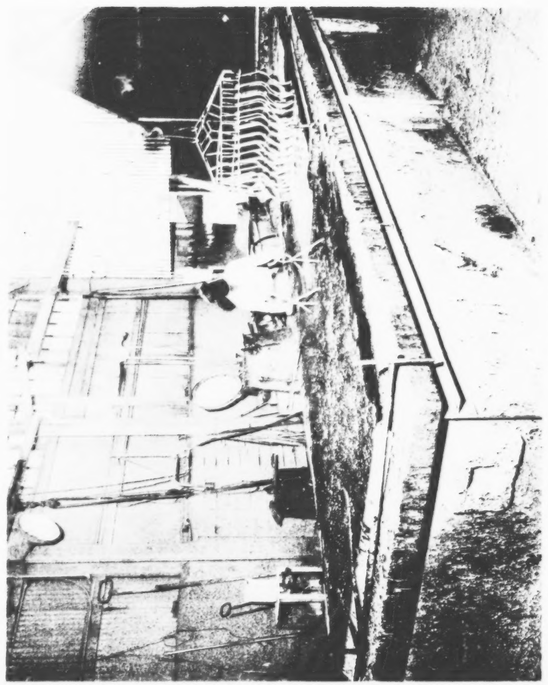

Figure 21. This photograph shows work being removed from a galvanizing kettle. The molten zinc bath is heated from below by a battery of gas-fired burners.

There are 27 of these kettles in Los Angeles County. The burners operate 24 hours per day to keep the metal molten for the dipping operations that are usually scheduled for 16 hours per day. NO_x emissions were found to be 0.018 pound per million Btu gross heating value. These emissions may also be evaluated as 0.013 pound per hour.

The total NO_x emissions for all galvanizing operations is 8 pounds or 0.004 ton per calendar day.

V. REFERENCES

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2. ASTM Method D 1608-58 T, "Tentative Method of Test for Oxides of Nitrogen in Gaseous Combustion Products (Phenoldisulfonic acid procedure)."

3. Based on unpublished data from Southern California Gas Company.

4. Data from Southern California Gas Company.

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6. Fay, H., Mohr, D. H., McDaniel, P. W., "Nitrogen Dioxide and Ozone Concentrations in Welding Operations," A.I.H.A. Quarterly, 18, pp. 19-28, March 1957.

7. Williamson, J. E. and Twiss, H. M., "Multiple-Chamber Incinerator Design Standards for Los Angeles County," Los Angeles County Air Pollution Control District.

8. Rose, A. H., Herrick, R. A., Horsely, R. R., and Stenburg, R. L., "Effects of Fuel Moisture and Incinerator Design on Effluents from Incinerators," Jour. A.P.C.A., 10, pp. 114-120, April 1960.